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XIV. *The Nature of the Nucleus in Hygroscopic Droplets.*
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1. INTRODUCTORY.

ALTHOUGH more than fifty years have elapsed since the existence of hygroscopic droplets in the atmosphere was first demonstrated by Aitken, yet still very little is known of their constitution and behaviour. It is generally supposed that a hygroscopic droplet consists of some millions of molecules of water which have condensed on, and dissolved, a hygroscopic centre, and a partial account can be given of the changes which the water part undergoes ⁽¹⁾. The number of water-molecules in a droplet which is neither growing nor evaporating is such that the vapour-pressure at its surface, depending chiefly on its radius of curvature and the molar concentration of the solution, is equal to the pressure of aqueous vapour in the surrounding air. Any inequality of vapour-pressure causes an exchange of water-molecules from the region of higher to that of lower pressure until equilibrium is restored. This process is either condensation or evaporation, according

* Communicated by Sir Oliver Lodge, D.Sc., F.R.S.

to its direction. Research in atmospheric electricity has led to the identification of hygroscopic droplets, when carrying an electric charge, with "large ions," and it has been deduced ⁽²⁾ that the radius of the latter is of the order of 4.5×10^{-6} cm. This, therefore, may be assumed to be the order of magnitude of a hygroscopic droplet in air of average relative humidity. With increasing humidity the droplet grows slowly, and when a state of supersaturation is attained growth takes place rapidly ⁽³⁾, until in fog the radius may reach a value of the order of 10^{-3} cm., in cloud of the order of 10^{-2} cm., and in rain up to nearly 0.2 cm.

Of the non-aqueous constituent of the droplet, the hygroscopic nucleus or solute, much less is known. In view of the apparently universal presence of chlorions in rainwater and in unpolluted river-water, it seems most probable that minute drops of sea-water projected into the air from breaking waves form a considerable source of hygroscopic particles. Köhler ⁽⁴⁾ has shown that in Arctic regions, where the risk of contamination from the products of civilization is very small, both rime and clouds contain appreciable amounts of chlorions, and that the actual size of cloud-droplets is of the order calculated for solutions of sea-salt, of the concentration found, at the vapour-pressure proper to the temperature, regard being had to the radius of curvature of the drop. By microscopical examination of the solid matter collected from suspension in air of coastal districts, J. S. Owens ⁽⁵⁾ has detected crystals similar in form and in hygroscopic properties to those of pure sodium chloride and of sea-salt. Although these crystals, of microscopic dimensions, are much larger than the nuclei of hygroscopic droplets, their existence shows that such salts are present in the air of at any rate some localities. Any hygroscopic substance dispersed through the air in a fine enough state for the Brownian movement to keep it in suspension for a sufficient length of time would, no doubt, act as a source of nuclei, but the range of probable substances in nature is limited.

The production of hygroscopic centres in the proximity of fires and flames generally cannot easily be explained as due to sea-salt. That nuclei in air passing through a flame are disintegrated, either by splitting of particles of salt, which is notoriously decrepitant, or by volatiliza-

tion of alkali chlorides, and then recondense as smaller nuclei is a plausible suggestion, and is supported by evidence of the ubiquity of sodium salts in air, shown by the continual splashes of yellow sodium flame seen whenever a Bunsen burner is lit. On the other hand, as the concentration of nuclei at sea is only some thousands per c.c. or less ⁽⁶⁾, whereas in cities ⁽⁷⁾ it is of the order of a hundred thousand per c.c., and as enhanced concentrations of nuclei are always found near sources of combustion, it seems likely that the nuclei of civilized countries, mainly, if not entirely, a by-product of combustion, are composed of substances other than sea-salt. It was with the view of identifying these other substances that the experiments to be described were undertaken.

As it is well known that sulphuric acid is very hygroscopic and therefore possesses in a marked degree the properties essential to atmospheric nuclei, and as it seems to be recognized ⁽⁸⁾ that some of the sulphur in fuel usually goes over to sulphur trioxide, although most of it is burned only to sulphur dioxide, our experiments were directed originally to the investigation of the production of nuclei from flames of fuel containing sulphur. We expected to find that when a fuel free from sulphur impurities was burned no yield of nuclei would be detected. When tested by experiment, however, this notion proved to be far from true, and the negative result led to subsequent experiments from which, as will appear, we ultimately conclude that the condensation nuclei of civilized lands are predominantly solutions of nitrous acid in droplet form.

2. Experimental Details.

The experimental work, which was conducted in a laboratory in central London during the winter months, consisted simply of determining the concentration of nuclei in an enclosed chamber, introducing various substances which it was thought might be possible sources of nuclei, and then re-determining the number of nuclei in the chamber to see whether the concentration had, in fact, increased. The methods adopted for the controlled production of nuclei may be divided into two broad categories: one in which nuclei were produced in the process of heating, not only by the combustion of fuels

but also by electrically heated wires and heated tubes ; the other in which nuclei were produced by spraying into the chamber sulphuric acid, sea-water, and various other liquids.

In most of our experiments the air tested for nucleation was drawn from a cubical wooden box, 72.5 litres in volume. This box had been designed for another purpose for which an approximately air-tight enclosure with smooth, easily cleaned walls and a side of transparent armoured plate glass was required. It was fitted with a door, fitting closely in grooves, and with a small powerful motor outside, used to drive a fan whereby the contents of the box could be mixed. Various apertures, which could be closed, served for the introduction or withdrawal of gases or other substances. A week before the box was brought into use the inner walls were smeared with glycerine to fix any dust-particles or soot likely to be produced in the course of our experiments.

Air was collected from the box and admitted into an Aitken Nucleus Counter through short lengths of rubber and glass tubing connecting a hole in the top of one corner with the intake nozzle of the counter, care being taken that air from the box and not merely from the tubing was brought into the counter. It was assumed, especially when the fan had been used, that the contents of the box were homogeneous, as no means of allowing for turbulence produced by burning fuel in the box was obvious. The details of experiments were varied as experience suggested the need for modification.

3. *Production of Nuclei by Combustion.*

With the object of seeing whether the production of nuclei by burning coal-gas might be attributed to the formation of sulphuric acid by oxidation of sulphur impurities in the gas, four different types of fuel were burned successively in the box : (1) ordinary coal-gas ; (2) gas which had been enclosed for a week in a large bottle over strong sodium hydroxide solution, which should remove at least part of the carbon disulphide and similar impurities ; (3) pure absolute alcohol ; and (4) a mixture of absolute alcohol and carbon disulphide, containing about the same proportion of sulphur as the unpurified coal-gas.

Before each experiment, counts were made of the number of nuclei in air taken from the box, which had been thoroughly ventilated, to confirm that the concentration in the box was the same as in the laboratory. Gas-flames were burned from drawn-out glass tubes introduced alight into the box and withdrawn after a few seconds. Liquid fuel was burned in a small porcelain capsule. In each case the duration of combustion was noted.

As soon as the contents of the box had settled down sufficiently after combustion was finished for the number of nuclei to be countable, usually after about half a minute, counts were begun. The smallest dilution in the Aitken counter ($1/1000$) was used but, even so, precipitation on the counting stage was sometimes so great as to be unreliable. With a precipitation of more than 10 drops per square, corresponding to a concentration of 10^9 nuclei per mm.³, it is not only difficult to count, but it is not certain that all the nuclei are precipitated. As it soon became evident that the concentration of nuclei after combustion had ceased was not constant, but diminished fairly rapidly with time, note was made of the times at which counts were made.

The results of this series of experiments are shown in Table I. The concentration of nuclei originally present in the box is shown in column 3, and in succeeding columns are given the concentrations 1, 2, 3 . . . minutes after combustion in the box had ceased. The unit of concentration of nuclei used throughout this paper is the number per cubic millimetre, the number in the box being about 72.5×10^6 times this number.

As may be seen from the table, the increase in the number of nuclei after combustion is in every case enormous, but the concentration falls off rapidly, the original number being reached in ten minutes or less.

Although the observations do not allow the rate of decay to be determined with certainty, and, indeed, it is unlikely that this rate should be constant, the concentration of nuclei is, roughly, inversely proportional to the time, and so mean values of the products (concentration of nuclei) \times (number of minutes since combustion ceased) are included in the table as an approximate indication of the efficacy of the various fuels as nuclear sources.

These values indicate (1) that the number of nuclei

TABLE I.
Concentration of Nuclei (number per mm.³) in an Enclosed Box before and after
Combustion of Various Fuels.

Material burned.	Duration of combustion.	Before.	After the number of minutes specified at the head of each column.										Mean values of (concentration) of nuclei \times (time).
			1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	
Pure absolute alcohol (0.1 cm. ³).....	27 secs.	95	210	180	130	70	85	85	110	115	—	—	481
Pure absolute alcohol (0.3 cm. ³).....	45 "	105	780	520	400	240	200	240	200	180	170	115	1194
CS ₂ and alcohol (1 in 250 by vol.)...	25 "	100	560	440	300	200	280	150	140	120	—	105	937
Purified coal-gas	5 "	83	380	270	130	120	60	90	—	—	—	—	438
Purified coal-gas	15 "	135	660	460	260	130	125	—	—	—	—	—	701
Commercial coal-gas (small flame)...	5 "	107	560	320	65	—	95	100	—	—	—	—	494
Commercial coal-gas (large flame)...	5 "	100	580	360	230	115	—	—	—	—	—	—	613
Commercial coal-gas	15 "	109	860	270	220	220	170	110	120	—	—	—	756

The values given are the means of 5 counts except those in column 3, which are the means of 20 counts or more.

produced by a flame depends on the duration of combustion; (2) that for the same duration of combustion slightly fewer nuclei are produced by a gas from which some of the sulphur has been extracted; (3) that the addition of carbon disulphide to pure alcohol considerably increases the number produced, the increased production raising the number to the same order as would be produced by coal-gas burning for the same time. These conclusions had been expected. The production of so many nuclei by burning pure absolute alcohol, completely free from sulphur impurities, was, however, unexpected, and prompted further investigation, as described in the following section.

In subsequent experiments no attempt was made to ensure, by thorough ventilation, that the concentration of nuclei in the box was the same as in the air of the room, as the latter was rather high; on the contrary, advantage was taken of the lower content in the box, which was probably due to the combined effects of coalescence and deposition. The concentration of nuclei in the room is included in the tables for the sake of comparison, although it has no direct bearing on the experiments.

The results of further experiments with a flame of commercial coal-gas are set out in Table II. They are substantially the same as in the earlier series, the introduction of the flame leading to large increases in numbers of nuclei, and the concentration falling off as time went on. It may be seen from the table that the rate of decay is, however, much slower than in the earlier experiments, the original number being reached only after some hours. This is in agreement with P. J. Nolan's observation⁽⁹⁾ that the rate of decay is higher when the number of nuclei is high than when only few are present, a fact which he attributes to coagulation being the main cause of decay in the initial stages and diffusion in the later.

4. Thermal Production of Nuclei without Combustion.

The formation of nuclei when pure absolute alcohol is burned suggests that heat alone is sufficient to produce nuclei from material already in the air, as it is difficult to see what product of combustion of alcohol could be nucleogenic. We decided, therefore, to experiment with

TABLE II.

Concentration of Nuclei in an Enclosed Box before and after Combustion of a Flame of Commercial Coal-gas.

Nov. 6th, 1933.	h m *	Nov. 7th.	h m	Nov. 7th.	h m
	11.15 $N_R = 420^*$		11.23 $N_R = 420$		14.23 $N_R = 140$
	12.15 $N_R = 200^*$		11.47 $N_0 = 13$		14.41 $N_0 = 14$
	14.27 $N_0 = 93$		12.05 Flame inserted for 10 secs.		14.50 Flame inserted for 20 secs.
	15.23 $N_0 = 56$				
	15.35 Flame inserted for 3 secs.		12.07 $N = 760^*$		14.52 $N = 290$
			12.08 $N = 260^*$		14.55 $N = 130$
	15.36 $N = 320^*$		12.10 $N = 140$		14.59 $N = 89$
	15.39 $N = 107$		12.14 $N = 61$		15.05 $N = 55$
	15.45 $N = 57$		12.18 $N = 47$		15.12 $N = 67$
			12.23 $N = 65$		15.23 $N = 41$
			12.35 $N = 47$		16.00 $N = 39$
			14.41 $N = 14$	Nov. 8th.	10.27 $N_R = 55$
					10.47 $N = 7$

* Mean of 5 determinations.

N_0 = Initial concentration of nuclei (number per mm.³) in the box.

N = Subsequent " " " "

N_R = Concentration of nuclei (number per mm.³) in the room.

Except where otherwise indicated the values given are the means of 20 determinations.

heat so applied that no external material, but only constituents of the air, could supply nuclei.

The first experiments of this series were conducted by introducing into the wooden box a coil of new nichrome wire connected with leads from the electric mains, a suitable variable resistance being included in the circuit. In these experiments the fan was disconnected, as the leads were passed through the orifice used for the spindle.

It was found that the number of nuclei in the box was greatly increased when the wire was heated even only to a dull redness, and that a preliminary heating of the wire for 13 minutes (to drive off any nucleogenic contamination) did not prevent a great increase in the number of nuclei. A similar experiment with a strip of carefully cleaned platinum foil instead of the nichrome also yielded a great increase of nuclei. The results of these experiments are shown in Table III.

When, however, an electric lamp was substituted for the wire or foil and heated, even for 20 minutes, no appreciable alteration in the number of nuclei was observed (Table III.), showing that a relatively high temperature was needed for the action.

In another experiment a length of Pyrex tubing, tightly plugged with cotton-wool at one end to filter out any nuclei from the air passing through it, and connected at the other end to the intake nozzle of the Aitken counter, was heated in the middle in a Bunsen burner. No increase in the number of nuclei was observed for a minute or two, but when the glass began to bend, and a sodium flame was observed, the number became too great to be counted.

It is well known that glowing bodies emit electrons, but in air these are short-lived, and would become attached to molecules or clusters of molecules to form small ions long before they reached the nucleus counter. It is extremely doubtful whether these small ions would be precipitated in the nucleus counter, as the supersaturation obtained therein is not sufficiently high to induce condensation on small ions when nuclei are present, as undoubtedly they were prior to heating. The copious production of nuclei in all these experiments points to the formation, concomitantly with electrons emitted from the heated surfaces, of other bodies which act as condensation nuclei. It was felt that other possibilities

TABLE III.
Concentration of Nuclei in an Enclosed Box before and after Electrical Heating of Metal Surfaces.

Nichrome Wire.			Platinum wire.		Electric lamp.
h m	$N_R = 44$	$N_0 = 23$	h m	$N_R = 121$	
Nov. 11th, 1933.	10.23	10.39	Nov. 14th.	10.03	Nov. 13th.
	$N_0 = 23$	10.51		$N_0 = 12$	$N_0 = 15$
	10.47 Wire heated for $1\frac{1}{2}$ min. (7.7 amps.)	11.05 Wire heated for $\frac{1}{2}$ min. (5.9 amps.)		10.30 Wire heated for $\frac{1}{2}$ min. (4.9 amps.)	$N_0 = 18$
	10.51 $N = 340$	11.07 $N = 220\frac{1}{2}$		10.33 $N = 270^*$	15.22 Current on for 2 min.
	10.55 $N = 120$	11.14 $N = 25\frac{1}{2}$		10.35 $N = 173$	15.26 $N = 15$
	11.47 $N = 39$	11.23 $N = 33$		10.38 $N = 43$	15.32 to 15.55 Current on continuously.
	12.15 $N = 39$	11.50 Wire heated for $1\frac{1}{2}$ min. (7.7 amps.)		10.42 $N = 23$	15.34 $N = 19$
		12.04 $N = 133$		11.03 $N = 21\frac{1}{2}$	15.53 $N = 15$
		12.17 $N = 28$		11.17 $N = 20.3$	
		12.34 $N = 22$			
		13.53 $N = 19$			

* Mean of 5 determinations.

 N_0 = Initial concentration of nuclei (number per mm.³) in the box. N = Subsequent " " " " N_R = Concentration of nuclei (number per mm.³) in the room.

Except where otherwise indicated the values given are the means of 20 determinations.

should be explored before the electronic explanation was accepted.

An alternative hypothesis is that nuclei in the immediate vicinity of the source of heat may be disintegrated to form smaller hygroscopic aggregates on which condensation would occur as they receded from the heated environment—the suggestion mentioned in the Introduction in discussing sea-salt nuclei. This hypothesis could be tested by conducting the same experiments in nucleus-free air, readily obtainable by aspirating air through a tightly packed filter of cotton-wool.

As the wooden box used hitherto was not adapted for the preparation or storage of nucleus-free air, further experiments were made in a large glass round-bottomed flask. Through a rubber stopper fitted into the flask were passed two thick copper wires, joined within the flask by a strip of clean platinum foil, as well as an inlet and an outlet tube. The wires could be connected to the electric mains, whilst the inlet was connected to two long tubes in series, both tightly packed with cotton-wool to remove nuclei by filtration. The outlet could be connected, as desired, either to a water-pump or to the Aitken counter. The whole system was made air-tight, except at the intake through the cotton-wool filter, by liberally covering all joints with plasticine. By means of the water-pump air was drawn through the flask until tests with the Aitken counter showed that the contents were free from nuclei. A current sufficient to heat the platinum to bright redness was then passed for 3 minutes and, after the current had been switched off, determinations of the number of nuclei were made. The mean number of nuclei from 20 counts was 420 per mm.³ Thus millions of nuclei had been produced in nucleus-free air.

Next, the platinum foil was heated for some time in order to drive off any possibly hygroscopic deposit and the experiment was repeated, nucleus-free air being introduced into the flask and the current then being switched on. Again numbers of nuclei, too great to be counted, appeared in the Aitken counter.

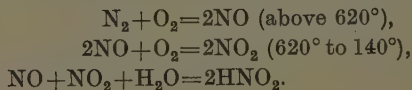
Evidently the hypothesis of disintegration of pre-existent nuclei does not alone account for the large numbers of nuclei produced by heat in air freed from nuclei. The following explanation appeared possible and was tested. The filters of cotton-wool, although they remove

nuclei, do not remove gases, such as sulphur dioxide. This gas, which would certainly be present in London air to the extent of about 0.1 volume per million, might be oxidized on the heated platinum surface by atmospheric oxygen to trioxide, which, with moisture in the air, would form hygroscopic droplets of sulphuric acid. In order to remove sulphur dioxide two sets of Geissler potash bulbs filled with potassium hydroxide solution were placed between the cotton-wool filters; the flask was freed from nuclei as before and a current was passed through the platinum foil. Again, however, nuclei were observed in great quantity.

The experiment was repeated with this difference, that one of the Geissler bulbs was filled with permanganate solution instead of potash. The permanganate solution would oxidize any sulphur dioxide present, leading to the formation of sulphuric acid which would be retained in the solution. After the usual procedure, however, a copious yield of nuclei was still observed.

Experience of the ease with which sulphur dioxide can be removed from air by "hyperol" solutions (a compound of hydrogen peroxide and urea) or by hydrogen peroxide itself, besides the ready solubility and oxidation of the gas in water, shows that it was impossible that washing with both alkali and a solution of an oxidizing agent should leave any in the air used for the experiments. It seemed clear that the nuclei found were produced from constituents of the purified air itself, viz., nitrogen, oxygen, and water-vapour.

It has been well known, since the time of Cavendish, that at the temperature of the electric spark oxygen and nitrogen will combine, producing finally oxides of nitrogen which will form soluble salts if the sparking is carried out over an alkaline solution, and the thermal combination of these gases has been studied by Nernst ⁽¹⁰⁾ and many others. The first product is nitric oxide, which, as it passes from the region of higher temperature to one below about 620° C., combines with another atom of oxygen, becoming nitrogen peroxide. The two oxides together will dissolve in water, forming nitrous acid:—



The third equation has been proposed by W. J. Müller ⁽¹¹⁾ as operating in the lead-chamber process of sulphuric acid manufacture.

In our experiments we had all the requisites for these reactions to occur, and on testing the air in the flask with the Griess-Ilosva reagent (which yields with nitrous acid, and with nothing else, a pink colour, owing to the diazotization of the amines in the reagent) a strong pink colour was obtained. Thus it is certain that nitrous acid was present in the flask, and the formation of hygroscopic droplets in this series of experiments seems almost certainly due to nitrous acid acting directly as a nucleogenic agent.

That nitrous acid is a normal constituent of the nuclei produced by flames was confirmed by testing, with the Griess-Ilosva reagent, the condensates formed, in some cases, on the outside of a round-bottomed flask through which cold water was circulating and beneath which a flame was burning, and in other cases on the inside of a bell jar placed over the flame. The flames used were (a) coal-gas in a Bunsen burner; (b) methylated spirit in a lamp; (c) tallow in a porcelain dish provided with a wick. In every case the presence of nitrous acid was detected.

The implications of the results of these experiments will be discussed later, in § 6.

5. Nuclei produced by Spray.

The remainder of the experimental work was concerned with the production of nuclei without the application of heat. At room temperatures various liquid substances were projected into the wooden box in the form of a fine spray, the electric fan being used to promote homogeneous dispersion in a fine state.

The first substance to be tested for nucleogenic properties was Nordhausen (fuming) sulphuric acid, minute quantities of which were blown into the box from a very fine capillary tube inserted through one of the small apertures. The results of this series of experiments are shown in Table IV., from which it may be seen that a copious production of nuclei was found in every case.

Similar experiments, wherein the sulphuric acid was replaced by a concentrated solution of hydrochloric

acid, were prompted by the well-known fact that when a bottle containing this liquid is shaken up and the stopper is removed fumes are observed around the stopper. In our experiments, however, as shown in Table IV., no yield of nuclei in the wooden box was found. In view of recent work by Jackson and Philip⁽¹²⁾, which indicates that ammonium chloride is an active nuclear source, it may be suggested in explanation of the fumes formed around the stopper that combination of hydrochloric acid with traces of ammonia present in the air may lead to the formation of ammonium chloride nuclei. That this process did not occur in the box may be because, as gas had been burned in the box on the previous day, acid gases or nuclei produced thereby had reacted with all the ammonia, none being left in the free state to combine with the hydrochloric acid.

In subsequent experiments the liquids were sprayed into the box by means of an ordinary glass scent-spray with a rubber ball, a cotton-wool plug being inserted in the air-vent in the bulb in order to filter out nuclei from any room-air entering the bottle. The liquids were sprayed into the wooden box through a small hole at one of the top corners, the glass tubing leading to the Aitken counter being temporarily removed and then replaced. The electric fan was in action while the liquids were being sprayed (except in one instance—Nov. 9th, 15^h 51^m—when by oversight the fan was not switched on until after the spraying).

The first liquid to be introduced into the box in this manner was sea-water, of full salinity, taken from the Thames estuary some months previously. The results of the observations, given in Table V., show that the number of nuclei in the box rose considerably after the spraying, although the increase was not nearly as great as in the case of sulphuric acid. That the increase is not due to room-air being introduced whilst spraying was in progress is shown by similar experiments with distilled water, the results of which are given in Table VI. With distilled water a slight increase in the number of nuclei was found, but it is relatively insignificant. It may be mentioned that at the conclusions of the set of experiments with sea-water, micro-organisms (moulds?) were observed on the cover-glass of the Aitken counter. These multiplied rapidly, and in two hours completely covered the view of the graticule.

TABLE IV.
Concentration of Nuclei in an Enclosed Box before and after introjecting $\text{H}_2\text{S}_2\text{O}_7$ or Concentrated Solution of HCl .

Nov. 8th, 1933.	$\frac{h}{m}$ 11.49	$N_0 = 7.8$ $\text{H}_2\text{S}_4\text{O}_7$ introduced	Nov. 15th.	$\frac{h}{m}$ 10.48	$N_0 = 6.3$ $\text{H}_2\text{S}_2\text{O}_7$ introduced	Nov. 15th.	$\frac{h}{m}$ 14.40	$N_0 = 12$ $\text{H}_2\text{S}_2\text{O}_7$ introduced	Nov. 8th.	$\frac{h}{m}$ 10.47	$N_0 = 7.1$
	12.00	$N = 125$		11.05	$N = 230^*$		14.58	$N = 27$		11.13	$N_0 = 7.4$
	12.07	$N = 43$		11.07	$N = 160$		15.27	$N = 22$		11.22	HCl introduced
	12.11	$N = 44$		11.11	$N = 93$		16.19	$N = 3.4$		11.25	$N = 7.3$
	12.20	$N_R = 46^\dagger$		11.14	$N = 27$	Nov. 16th.	12.02			11.42	HCl introduced
	12.25	$N = 15^\dagger$		11.17	$N = 23$						
	12.39	$N_R = 320$		11.25	$N = 24$						
Nov. 9th.	10.23	$N = 9$		11.35	$N = 20$						
	11.00			11.41	$N = 20$						
				12.29	$N = 20$						
				13.56	$N = 12$						
				14.40						11.45	$N = 7.8$

* Mean of 5 determinations.

N_0 = Initial concentration of nuclei (number per mm^3) in the box.

N = Subsequent " " " " " "

N_R = Concentration of nuclei (number per mm^3) in the room.

Except where otherwise indicated the values given are the means of 20 determinations.

TABLE V.

Concentration of Nuclei in an Enclosed Box before and after spraying Sea-water.

Nov. 9th, 1933.	h m	Nov. 9th.			Nov. 10th.		
		h m	$N_R = 520^*$	$N_0 = 8.8$	h m	$N_0 = 8.8$	h m
11.00	$N_R = 9$	13.16	$N_R = 520^*$	$N_0 = 8.8$	15.43	$N_0 = 8.8$	$N_R = 187$
11.25	$N_0 = 12$	13.23	$N_0 = 8.8$		15.51	90 pumps of sea-water	$N_0 = 9.3$
11.35	10 pumps of sea-water	13.32	30 pumps of sea-water		15.55	$N = 36^*$	20 pumps of sea-water
		13.35	$N = 38\dagger$		15.57	$N = 30^*$	$N = 19.5\dagger$
11.39	$N = 23$	13.38	$N = 25$		15.59	$N = 22$	$N = 18.5$
11.43	$N = 12$	13.42	$N = 18$		16.02	$N = 13^*$	$N = 14$
12.21	$N = 8.8$	13.53	$N = 16$		16.23	$N = 13\dagger$	
		14.20	$N = 14$		Nov. 10th.	$N = 9.3$	
		14.51	$N = 12$				
		15.11	$N = 10\dagger$				
		15.43	$N = 8.8$				

 N_0 = Initial concentration of nuclei (number per mm.³) in the box. N = Subsequent " " " " " " N_R = Concentration of nuclei (number per mm.³) in the room.

* Mean of 5 determinations.

† " 10 "

† " 15 "

Except where otherwise indicated the values given are the means of 20 determinations.

TABLE VI.
Concentration of Nuclei in an Enclosed Box before and after spraying Distilled Water.

	h	m		h	m		h	m
Nov. 10th, 1933.	15.21	$N_R = 129$	Nov. 14th.	14.40	$N_0 = 8$	Nov. 14th.	15.20	$N_0 = 11$
	15.32	$N_0 = 10$		14.42	13 pumps of distilled water		15.21	20 pumps of distilled water
	15.55	$N_0 = 7$		14.45	$N = 11$		15.29	$N = 12$
	16.01	10 pumps of distilled water		15.20	$N = 11$			
	16.03	$N = 9$						

TABLE VII.
Concentration of Nuclei in an Enclosed Box before and after spraying Solutions of NaOH or KOH.

Caustic soda.			Caustic potash.		
	h	m		h	m
Nov. 16th, 1933.	12.02	$N_0 = 3.4$	Nov. 17th.	14.15	$N_0 = 3.7$
	12.17	$N_0 = 3.8$		14.17	13 pumps of strong KOH
	12.23	10 pumps of dilute NaOH		14.21	$N = 2.1$
	12.25	$N = 4.3$			
			Nov. 17th.	14.21	$N_0 = 2.1$
				14.28	20 pumps of strong KOH
				14.32	$N = 3.6$

N_0 = Initial concentration of nuclei (number per mm.³) in the box.

N = Subsequent " " "

N_R = Concentration of nuclei (number per mm.³) in the room.

The values given are the means of 20 determinations.

Various other liquids were tested. The results for caustic soda and caustic potash, given in Table VII., show no appreciable increase in the number of nuclei after spraying. Calcium chloride solution, on the other hand, gave a small but quite definite increase. Tap-water was found, as was expected, to be but a feeble producer of nuclei.

The negative results with caustic alkalis are somewhat surprising, since it seems certain that, as the vapour-pressure of a solution is always less than that of the pure solvent, any solution having an appreciable osmotic pressure should act as a nucleus. It may be, however, that only a few of the drops impelled into the air from a sprayer are small enough to remain in suspension; and that these soon absorb enough water to fall rapidly. It may be remarked that, in the course of spraying caustic potash, the nozzle of the sprayer tended to become choked owing to the formation of carbonate, and it was noticed afterwards that crystals of potassium carbonate had also formed around the aperture in the box through which the solution was sprayed.

The main interest of these experiments lies in the positive results obtained with fuming sulphuric acid and with sea-water, and for the present purpose there seemed no object in devising a more satisfactory technique.

6. *Discussion of Results.*

We have shown that in addition to sea-salt—which the presence of chlorides in rime, cloud, snow, and rain, as well as in all natural waters found on the earth's surface in places where contamination with urine (which has a high chlorion content) is unlikely, indicates as the most usual hygroscopic constituent of nuclei in nature—nuclei can also be formed from other hygroscopic substances. Of these, nitrous and sulphuric acids seem the most important, for reasons to be set out.

The atmosphere contains abundant material for the formation of nitrous acid—nitrogen, oxygen, and water-vapour—and it is known that under suitable conditions of temperature the reactions necessary for its formation do occur. Our experiments show that the conditions leading to the formation of nitrous acid lead also to the formation of nuclei. Although the identity of the two

is not a matter of fact, it is a very strong probability, and there is ample evidence which may be adduced in support of it.

The existence of traces of nitrous acid in the air is well known, or rather, perhaps, well established. It has frequently been mistaken for ozone, or for "antozone," owing to its behaviour with iodides, but the production of a pink colour whenever the Griess-Ilosva reagent is exposed for long to the air, and the ease with which nitrous acid can be detected in rain, show that it is a frequent constituent of air. In the air of St. James's Square, London, Francis and Parsons⁽¹³⁾ found from 0.03 to 16.8 (the latter value in a fog) parts per million by volume calculated as NO_2 , equivalent to from 0.6 to 35.4×10^{-11} gm. per c.c. of nitrous acid. These authors, in discussing the methods used by them and others for determining nitrous acid (*loc. cit.* p. 270), state: "Experiments in the course of this work had shown that any process of scrubbing was likely to fail in removing oxides of nitrogen completely from air." This fact, which we can confirm, points to the existence of the oxides in two states—gas or vapour, which is readily absorbed, and a liquid or solid phase, which is not extensively absorbed, the droplets or particles making relatively few collisions with the surface of the absorbent owing to the relatively slow Brownian movement. We have found nitrous acid in water condensed from air bubbled through a solution of hyperol, which, in addition to removing sulphur dioxide should certainly also absorb nitrous acid or its anhydride *if in gaseous form*, either oxidizing it or liberating its nitrogen. These facts indicate the existence in air of nitrous acid in liquid form, and in this form the droplets would be, in effect, condensation nuclei.

Striking confirmation of the conclusion that nitrous acid causes condensation is to be found in a paper by E. Pringal⁽¹⁴⁾, who remarked that the mists formed, either spontaneously or by forced condensation (*i. e.*, by adiabatic expansion), in air, nitrogen, oxygen, and hydrogen, after ozonization, might reasonably be attributed to the formation of nitrous gases by the oxidation of traces of nitrogen, or by combination of nitrogen with traces of oxygen as the case may be, or, in air, by oxidation of its nitrogen. His reasoning was based on the fainter mists formed in the purer gases, and on the

lessening of the mist when the ozonizer was followed by a tube of alkaline solution to absorb the nitrous acid which had been formed. Briefly, the less the probable amount of nitrous acid the fainter the mist. Pringal's main object was to show that ozone itself did not cause nucleation, and he did not confirm directly the presence of nitrous acid. Pringal adduces an observation of J. Kiessling on the Lake of the Four Cantons as an example in nature of this action of nitrous acid formed in an electric field:—

“Unmittelbar nachdem aus einer auf dem Uri Rostock lagernden nach unten hin schaft begrenzten Gewitterwolke ein sehr hell leuchtender Blitz fast senkrecht zum Seenniveau sich entladen hatte, konnte ein genau der Blitzbahn entsprechender, schmaler grauer Regenstreifen beobachtet werden, der 8–10 Secunden lang sich sehr deutlich von den dunkel, violett erscheinenden Felswänden abhob.”

The case for sulphuric acid nuclei is not so clear. Since all fuels contain sulphur, even vegetable fuels such as twigs, branches, peat, etc., inasmuch as sulphur appears to be a constant constituent of proteins ⁽¹⁵⁾, it follows that the process of combustion is inevitably attended by formation of sulphur dioxide. Indeed, it is well known that sulphur dioxide is a common constituent of town air, and its concentration, which is, however, usually less than one in a million volumes, is determined at many places in this country by methods set forth by the Government Research Committee on Atmospheric Pollution, based on that developed by G. H. Bailey ⁽¹⁶⁾. It does not appear, however, that oxidation of sulphur dioxide by atmospheric oxygen in the gas phase occurs at all readily, and if oxidation only goes on in solution this presupposes the existence of droplets in the air, in which case sulphuric acid cannot be considered as the *source* of nuclei in the atmosphere generally. The presence of nitrous acid nuclei in air would furnish an oxidizing agent, as in the chamber process of manufacture of sulphuric acid, and at present it seems most likely that, when sulphuric acid nuclei are formed, their genesis is brought about by oxidation of sulphur dioxide absorbed by nitrous acid nuclei already existing.

The detection of sulphuric acid in air, or in condensates obtained by cooling air saturated with water-vapour, is by no means easy, as its presence in liquid form prevents

its ready absorption by reagents, and attempts at filtration, *e. g.*, through sintered glass or asbestos, are likely to be complicated by the simultaneous collection of alkaline particles of calcium carbonate from the erosion of building materials, or of the ashes of plants in a bonfire, causing sulphates, and not the free acid, to be detected. Moreover, the appreciable solubility of barium sulphate makes detection of very small amounts of the SO_4^{2-} ion difficult. Nevertheless, one of us, with G. B. Courtier, has obtained some evidence of the presence of sulphuric acid in air in amounts of the order of one per cent. of the sulphur found as dioxide. In this work, which is not yet completed, air freed from sulphur dioxide, by being bubbled through hyperol solution, was cooled by being passed through a vessel surrounded with ice. Condensed water was yielded which had a lower pH than if it were acid only with carbon dioxide, and which, after the addition of barium chloride and concentration, gave crystals indistinguishable, under the microscope, from barium sulphate. The condensed water also contained both nitrites and chlorides, suggesting that all three probable sources of nuclei were involved. Further experiments in which sulphur dioxide was removed by lead peroxide have, in some cases, yielded sulphuric acid. In these experiments the use of lead peroxide instead of hyperol eliminated the possibility of SO_2 being oxidized by hydrogen peroxide vapour in the gas phase, and yielding sulphuric acid which would pass through hyperol unabsorbed and, when condensed, might be considered as having been present in the air originally. All these experiments were made on London air containing SO_2 in amounts of the order of 0.1 to 0.6 volumes per million, and the amounts of H_2SO_4 found varied from 4 to 20×10^{-12} gm. per c.c. The higher results were usually associated with fog and the lower ones with rain.

Quantitative considerations prompt the following questions. What concentrations of sulphuric or nitrous acids would be required to produce, say, 100,000 nuclei per c.c., and do these acids exist in air in concentrations of the required order?

If the average radius of a nucleus, assumed to be spherical, is 5×10^{-6} cm., the volume occupied by 100,000 nuclei is 5×10^{-11} c.c., and if the whole of this volume is assumed to be sulphuric acid of density 1.8,

their weight would be 9×10^{-11} gm. This corresponds to the oxidation of about 2×10^{-8} c.c. of SO_2 , or 0.02 volumes per million volumes of air. But consideration of the vapour-tension of mixtures of water and sulphuric acid shows that at as high a temperature as 25°C . air of 75 per cent. relative humidity would be in equilibrium with acid of about 33 per cent. strength. As the density of this is 1.25, the amount of sulphuric acid would be only 2×10^{-11} gm., corresponding with the oxidation of 0.0047 volumes per million of sulphur dioxide, which is considerably less than the concentration of this gas found in London air. Thus ample material is available for the formation of sulphuric acid nuclei. That there is, in fact, an excess of material points to difficulty in effecting oxidation. If this depends on random collisions between molecules of sulphur dioxide gas and nitrous acid nuclei, the process will necessarily be slow.

The properties of nitrous acid are not known, but having regard to its molecular weight and to the density of nitric acid, it is reasonable to assume that the amount needed to account for 100,000 nuclei would be of the same order as for sulphuric acid, about 10^{-11} or 10^{-10} gm. This is of the order equivalent to the amounts of NO_2 found by Francis and Parsons, as stated above.

In conclusion, it may be noted that A. R. Hogg⁽¹⁷⁾ has recently suggested the existence of two distinct types of hygroscopic nuclei in order to explain the presence of large and intermediate ions found in the air at Canberra. Owing to its small density of population, Australia is a continent where sea-water nuclei are not likely to be drastically outnumbered by the nitrous and sulphuric acid nuclei formed by the industrial and domestic fires of populous areas. In fact the presence, if not the preponderance, of sea-water nuclei is likely to be the rule there rather than the exception. By comparing observations on days respectively free from and associated with bush-fires, Hogg finds that small ions combine less quickly with the nuclei normally found than with those produced by the fires. As the rate of combination depends on the surface area of nuclei, this implies that normal nuclei are smaller, and therefore more mobile, than the fire-produced ones. That is, the intermediate ions, of higher mobility, are likely to

be normal, or sea-water nuclei, while the larger, slowly moving, ions are likely to be nitrous, or sulphuric acid. It may be remarked, that if this hypothesis proves to be correct, it implies that, for the same humidity, fire-produced nuclei are much larger than sea-water nuclei, the diameters, deduced from values of mobility, being of the order of 8×10^{-6} and 8×10^{-7} cm. respectively. This conclusion is supported by consideration of the relative hygroscopicity of sea-salt and sulphuric acid, which suggests that, for approximately the same number of molecules of hygroscopic substance in a droplet, sulphuric acid droplets would be very much larger than those of the salt-mixture. It appears most probable that nitrous acid, which is only known in solution, would also be much more hygroscopic than sea-salt.

It may be remarked that the identification of intermediate ions with sea-water nuclei and of large, or Langevin, ions with fire-produced nuclei would explain why the latter have been found so extensively in Europe, where combustion is general, and the former but rarely.

7. *Appendix.*

Since the above was written, Dr. G. C. Simpson has called our attention to a paper, published in 1887, by R. v. Helmholtz ⁽¹⁸⁾ in which, after first describing the accelerated and intensive condensation produced in a jet of steam issuing from a tube of 1 to 2 mm. opening by bringing near it an electrified point, he shows by experiments with the jet and by others in a "Nebel-apparat," equivalent to a Wilson chamber, that the then obvious explanation of the formation of nuclei by dust being attracted, charged, and then repelled, by the electrified point did not hold. This fallacy is now of course well known.

Helmholtz experimented with heated platinum and other metals, and found them to be, above red heat, prolific producers of nuclei both in the open, as shown by their effect on the steam-jet, and also in the condensation chamber. Flames of coal-gas, carbon monoxide, hydrogen, stearin, and turpentine, whether smoky or clear, were active.

Sulphuric acid, other mineral acids, including hydrochloric and solutions of salts, especially ammonium

chloride, were active when sprayed into the steam-jet. All glowing bodies were also active.

An alcohol flame, however, did not produce visible cloud or fog unless particles of sodium coloured it. The catalytic action of platinum on alcohol was also unsuccessful in producing clouds. In view of the undoubted formation of nuclei in our experiments when an alcohol flame was burned, we are inclined to explain this result of Helmholtz by his reliance on the absence of a visible fog as evidence of inactivity instead of on actual counts in the Aitken apparatus.

Helmholtz's explanation of the phenomena is not very convincing. Having found that ozone could not be detected by starch iodide paper near the electrified point, and concluded, on other sound evidence, that "Ozon wenigstens in seiner (dreiatomige Dauerform nicht wirksam ist" (*cf.* Pringal, quoted above), he seems to have assumed that the tetramethyl-phenylene-diamine paper introduced by Wurster was a specific test for "Antozon" or monatomic oxygen, and on this bases a rather vague electro-chemical theory. On consulting Wurster's published work ⁽¹⁹⁾, however, we find that he laments that his tests are not specific for any one oxidizing substance. "Leider giebt mein Papier, besonders das Tetramethylparaphenylenediaminpapier *keine* ganz definitive Entscheidung, ob die auf der Haupt entstehende Färbung durch Wasserstoffsperoxyd oder salpetrige Säure bedingt wird Bei salpetrigen Salzen tritt die intensive Färbung, sofort ein."

In this work, carried out nearly fifty years ago, Helmholtz effectively disproved the dust and ozone theories of nucleus formation and showed that air in the neighbourhood of flames or glowing bodies contained an oxidizing constituent which gave rise to nuclei. Had he made specific tests for nitrous acid we believe he would have found it.

We are greatly indebted to Dr. Simpson for calling our attention to this work and for many helpful suggestions and criticisms in discussing our own results. One of us desires also to express his thanks to Dr. Simpson for permission to carry out the investigation and to publish the results, and to Professor Brunt for his encouragement and continued interest.

Summary.

Comparison of the concentration of nuclei in an enclosed box before and after the combustion of various fuels, and the electrical heating of metal surfaces, within the box, showed that formation of nuclei occurred under suitable conditions of temperature whatever the source of heat, even when a flame of pure absolute alcohol was burned and when a platinum surface was heated in air freed from pre-existent nuclei and from sulphur dioxide and other acid gases. Of the hypotheses which may be advanced in explanation, the only one which appears to cover all the facts is that nitrous acid droplets are formed from constituents of the air under suitable conditions of temperature. The existence of nitrous acid was detected in the nucleus-free air in which the platinum surface was heated. It was also detected in the condensates obtained from air collected from various flames.

Determinations of the concentration of nuclei in the box before and after spraying various liquids showed that fuming sulphuric acid and sea-water were active producers of nuclei, whilst the other liquids tested were inactive or at most relatively feeble producers.

Reasons are given for the belief that, although sea-water is the chief constituent of nuclei in nature, most of the nuclei produced in civilized countries by the fires, furnaces, etc., associated with human activity are droplets of nitrous acid, some of sulphuric acid probably being formed also.

References.

- (1) M. G. Bennett, *Q. J. R. Met. Soc.* lx. pp. 3-14 (1934).
- (2) Sir J. J. Thomson and G. P. Thomson, 'Conduction of Electricity through Gases,' pp. 187-89. Camb. Univ. Press (1928).
- (3) H. Köhler, *Med. från Statens Met.-Hydrogr. Anstalt*, iii. 8, pp. 1-16 (1926).
- (4) H. Köhler, *Geofys. Publ.* ii. 1, pp. 1-15 (1923).
- (5) J. S. Owens, *Proc. Roy. Soc. A*, cx. pp. 738-52 (1926).
- (6) A. Wigand, *Ann. Hyd. Berlin*, lviii. pp. 212-16 (1930).
- (7) J. Aitken, *Coll. Sci. Papers*, p. 236. Camb. Univ. Press (1923).
- (8) G. W. Hewson, S. L. Pearce, A. Pollitt, and R. L. Rees, *J. C. S. I.* 1933.
- (9) P. J. Nolan, *Proc. R. Irish Acad.* xli. pp. 61-69 (1933).
- (10) W. Nernst, *Chem. Centr.* ii. p. 1368 (1904), and *K. Ges. Wiss. Göttingen*, pp. 261-76 (1904).
- (11) W. J. Müller, *Z. angew. Chem.* xlv. p. 821 (1931), and *Z. anorg. u. allgem. Chem.* iii. pp. 218, 307-13.
- (12) C. N. Jackson and J. C. Philip, *Journ. Chem. Soc.* 1934, pp. 341-47.

- (13) A. G. Francis and A. T. Parsons, *The Analyst*, l. pp. 262-72 (1925); see also G. Defren, *Chem. News*, lxxiv. pp. 230-31, 240, 241 (1896), and W. Hayhurst and J. N. Pring, *Trans. Chem. Soc.* xvii. pp. 868-77 (1910).
- (14) E. Pringal, *Ann. Physik*, xxvi. 4 pp. 727-50 (1908).
- (15) M. Kohn and F. G. Goodridge, 'Sulphur Metabolism,' pp. 399, 754, tab. 598.
- (16) G. H. Bailey, J. B. Cohen, and A. J. Hartog, *Proc. Manc. Field Nat. Soc.* (1891); see also B. A. Ellis, *The Investigation of Atmos. Poll.* xvii. Report, 1931, App. i. pp. 38-49.
- (17) A. R. Hogg, *Gerl. Beitr. z. Geophys.* xli. pp. 1-57 (1934).
- (18) R. von Helmholtz, *Ann. d. Physik. u. Chem.* xxxii. pp. 1-19 (1887).
- (19) C. Wurster, *Ber. Deut. Chem. Ges.* xix. pp. 3195, 3206, 3208 (1886).

XV. On the Theory of Electron Scattering by Atoms.

By M. GHOSH, *M.Sc., A.Inst.P.**

THE study of the phenomenon of elastic scattering of the electron was made by a number of workers both theoretically and experimentally. Rutherford ⁽¹⁾ first deduced dynamically an expression for the intensity of scattering; but his formula fails to explain the scattering phenomenon at all angles and for all electron velocities. It gives much larger value of the intensity at small angles than the observed value. Following the wave mechanical method Born ⁽²⁾ derived a formula for intensity by solving the wave equation of the system in terms of an incident plane-wave and a number of spherical waves corresponding to the incident and scattered particles respectively by successive approximations. His formula also bore the same fate. It gives much lesser value than what is observed at small angles and cannot explain the experimental values for large angles and for small velocities. He, however, neglected the effect of exchange, which was afterwards pointed out by Oppenheimer ⁽³⁾. Mott ⁽⁴⁾, using Coulombian field, has deduced an expression similar to Rutherford. The only difference lies in the choice of the atomic number Z , for which Mott takes $Z - F(\theta)$ where $F(\theta)$ is according to him the structure factor depending on the angle of scattering. Hughes and his coworkers ⁽¹²⁾ have tried to explain their observations by Mott's formula,

* Communicated by Prof. K. C. Kar, D.Sc.

where the structure factor is determined for different angles, by exactly fitting a set of the observed values to the theoretical expression. Comparison with different sets are made by taking into account this set of structure factor. In each case the curve for the observed value is steeper than what is obtained from the expression given by Mott. An expression for the intensity of scattering for the fast electron was also deduced by Mott ⁽⁴⁾ by using Dirac wave equation. Attempt was made to explain Dymond's ⁽⁵⁾ experimental curve by Mott's deductions by using Hartree field. Bullard and Massey ⁽⁶⁾ have derived an expression for the same by assuming Fermi-Thomas distribution of potential field. None of the theories cited above can explain fully the behaviour of the electron scattering, especially in the case of the slow electron, where the intensity of scattering passes through maximum and minimum, as is observed by Arnot and others ⁽⁷⁾. Faxen and Holtzmark ⁽⁸⁾ developed a wave mechanical method for calculating the intensity of scattering of the electron wave by a given static field, following the method used by Rayleigh in his treatment of the scattering of sound-wave by obstacles. Later on Allis and Morse ⁽⁹⁾ cleverly eliminated the algebraical difficulty present in Faxen and Holtzmark's derivation, and made computation with the experimental data by suitable adjustment of parameters. MacDougall ⁽¹⁰⁾ also calculated the same for helium and hydrogen by using Hartree field in Allis-Morse's model. Massey and Mohr ⁽¹¹⁾ have tried to extend the Oppenheimer's theory by considering the electron exchange and distorsion of the electron wave, and arrived at the conclusion that the effect of exchange and distorsion must not persist to quite high velocities of the electron, but promises to explain the scattering at large angles and small velocities. They have further introduced polarization effect in order to explain the marked excess of scattering observed at small angles above what is given by Born's approximation.

In the present paper we shall try to develop a wave statistical formula for scattering, taking into account the *excluded phase-space* of the scattered electron. *The foreign electron while moving does not penetrate up to the centre of the scattering element, but leaves a spherical space round it the radius of which gives the critical approach of the*

electron to the atomic system*. We shall therefore introduce this critical approach (r_0) as the lower limit of r -integration of phase-space. It may be pointed out here that though the investigation we are going to undertake may be mainly based upon Born's method to the first-approximation, with the correction for the excluded phase-space, yet its validity cannot be questioned. It is of course clear that further improvement of the present theory, if necessary, may be sought afterwards in the direction of the exchange, distorsion, and polarization effects.

The electron beam is assumed to be incident on the atomic target from the negative x axis, and is assumed to scatter elastically; further, all orbital Z-fold electrons of the atom, for the simplification of the problem is taken to be united in K-shell without interference to one another. The Z-fold positively charged nucleus of the neutral atom is somewhat screened, due to the presence of the negatively charged electron shell, which takes the value \bar{Z} , and is less than Z by the amount of screening. The potential energy between the incident electron and the atomic system including the nucleus and the electrons in K-shell is taken in the usual form

$$V = e^2 \bar{Z} \left(\frac{1}{r} - \frac{1}{a} \right) \exp(-Cr), \quad \dots \quad (1)$$

where r is the distance of the moving electron from the centre of the nucleus which is taken as the origin of the axes of reference and $C = \frac{2}{a}$, a being the radius of the K-shell of the atom.

The relativistic χ_1 , wave-equation of the incident-electron neglecting its spin⁽¹⁴⁾, is

$$\Delta \chi_1 + \frac{4\pi^2}{\hbar^2 c^2} \{ (E - V)^2 - E_0^2 \} \chi_1 = 0, \quad \dots \quad (2a)$$

where

$$E = m_0 c^2 \left(1 - \frac{v^2}{c^2} \right)^{\frac{1}{2}}; \quad E_0 = m_0 c^2. \quad \dots \quad (2b)$$

* This idea was first suggested by Mukherjee⁽¹³⁾ in his interesting paper on anomalous α -scattering.

The notations have got their usual meaning. Here V is taken as the perturbation term.

Now

$$\chi_1 = \chi_{1,0} + \chi_{1,1} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$\chi_{1,0}$ is the unperturbed wave and $\chi_{1,1}$ is the amount introduced due to the perturbation produced by the atomic field.

From (3) equation (2) can be written in the form

$$\Delta \chi_{1,0} + k^2 \chi_{1,0} + \Delta \chi_{1,1} + k^2 \chi_{1,1} = -\frac{4\pi^2}{\hbar^2 e^2} (V^2 - 2EV) \chi_{1,0}.$$

Since the first two terms taken by themselves vanish, we have

$$\Delta \chi_{1,0} + k^2 \chi_{1,0} = 0, \quad . \quad . \quad . \quad . \quad (4a)$$

$$\Delta \chi_{1,1} + k^2 \chi_{1,1} = -\frac{4\pi^2}{\hbar^2 c^2} (V^2 - 2EV) \chi_{1,0}, \quad . \quad . \quad (4b)$$

where
$$k^2 = \frac{4\pi^2}{\hbar^2 c^2} (E^2 - E_0^2). \quad . \quad . \quad . \quad . \quad (4c)$$

The solution of the above equations, on substituting the value of V from (1), are given by

$$\chi_{1,0} = e^{ikz}$$

$$\begin{aligned} \chi_{1,1} = & \frac{e^{ikr}}{r} \left[\frac{2\pi e^2 Z E}{\hbar^2 c^2} \int_0^{2\pi} \int_0^\pi \int_{r_0}^\infty \left(\frac{1}{\rho} - \frac{1}{a} \right) e^{-(C - iD \cos \phi)\rho} \right. \\ & \times \rho^2 d\rho d(\cos \phi) d\psi - \frac{\pi e^4 Z E^2}{\hbar^2 c^2} \int_0^{2\pi} \int_0^\pi \int_{r_0}^\infty \left(\frac{1}{\rho} - \frac{1}{a} \right)^2 \\ & \left. \times e^{-(2C - iD \cos \phi)\rho} \rho^2 d\rho d(\cos \phi) d\psi \right], \quad . \quad . \quad . \quad . \quad (5) \end{aligned}$$

where

$$C = \frac{2}{a}; \quad D = 2k \sin \frac{\theta}{2}. \quad . \quad . \quad . \quad . \quad (6)$$

θ being the angle of scattering. The lower limit of ρ integration is taken r_0 for reasons stated before.

So

$$\begin{aligned} \chi_{1,1} = & \frac{e^{ikr}}{r} \left[\frac{4\pi^2 e^2 Z E}{\hbar^2 c^2} \left(I_1 - \frac{1}{a} I_2 \right) \right. \\ & \left. - \frac{2\pi^2 e^4 Z^2}{\hbar^2 c^2} \left(I_3 - \frac{2}{a} I_4 + \frac{1}{a^2} I_5 \right) \right], \quad . \quad (7) \end{aligned}$$

where

$$I_1 = \int_0^\pi \int_{r_0}^\infty \rho \exp \{-(C-iD \cos \phi)\rho\} d\rho d(\cos \phi) \\ = -\frac{2e^{-Cr_0}}{D(D^2+C^2)} \{D \cos Dr_0 + C \sin Dr_0\}. \quad (8a)$$

$$I_2 = \int_0^\pi \int_{r_0}^\infty \rho^2 \exp \{-(C-iD \cos \phi)\rho\} d\rho d(\cos \phi) \\ = -\frac{2e^{-Cr_0}}{D(D^2+C^2)} \left[D \left(r_0 + \frac{2C}{D^2+C^2} \right) \cos Dr_0 \right. \\ \left. + C \left(r_0 + \frac{C^2-D^2}{C(D^2+C^2)} \right) \sin Dr_0 \right], \quad (8b)$$

and

$$I_3 = \int_0^\pi \int_{r_0}^\infty \exp \{-(2C-iD \cos \phi)\rho\} d\rho d(\cos \phi) = 0, \quad (8c)$$

and I_4, I_5 are obtained by putting $2C$ for C in I_1 and I_2 respectively.

From (8) equation (7) can be written

$$\chi_{1,1} = -\frac{4\pi^2}{\hbar^2 c^2} \cdot \frac{E}{4k^2} e^{2Z} \frac{e^{ikr}}{r} \cdot \frac{2e^{-Cr_0}}{\sin^2 \theta/2 + \alpha^2} \\ \times \left[\left\{ \left(1 - \frac{r_0}{a} - \frac{\alpha^2}{\sin^2 \theta/2 + \alpha^2} \right) + \frac{e^{2Z}}{Ea} e^{-Cr_0} \right. \right. \\ \times \left(1 - \frac{r_0}{2a} - \frac{\alpha^2}{\sin^2 \theta/2 + 4\alpha^2} \right) \frac{\sin^2 \theta/2 + \alpha^2}{\sin^2 \theta/2 + 4\alpha^2} \Big\} \\ \times \cos Dr_0 + \frac{C}{D} \left\{ \left(1 - \frac{r_0}{a} + \frac{\sin^2 \theta/2 - \alpha^2}{2(\sin^2 \theta/2 + \alpha^2)} \right) \right. \\ \left. + \frac{2e^{2Z}}{Ea} e^{-Cr_0} \left(1 - \frac{r_0}{2a} + \frac{1 \sin^2 \theta/2 - 4\alpha^2}{8 \sin^2 \theta/2 + 4\alpha^2} \right) \right. \\ \left. \times \frac{\sin^2 \theta/2 + \alpha^2}{\sin^2 \theta/2 + 4\alpha^2} \Big\} \sin Dr_0 \right], \quad \dots \dots (9)$$

where

$$\alpha = \frac{C}{2k} = \frac{1}{ak}.$$

On putting the value of E and k we have for intensity

$$\begin{aligned}
 |\chi_{1,1}|^2 = & \frac{e^4 Z^2}{4m_0^2 v^4} \left(1 - \frac{v^2}{c^2}\right) \frac{e^{-2Cr_0}}{(\sin^2 \theta/2 + \alpha^2)^2} \\
 & \times \left[\left\{ \left(1 - \frac{r_0}{a} - \frac{\alpha^2}{\sin^2 \theta/2 + \alpha^2}\right) + \frac{e^2 Z^*}{m_0 c^2 a} \right. \right. \\
 & \times \left(1 - \frac{v^2}{c^2}\right)^{\frac{1}{2}} e^{-Cr_0} \left(1 - \frac{r_0}{2a} - \frac{\alpha^2}{\sin^2 \theta/2 + 4\alpha^2}\right) \\
 & \times \frac{\sin^2 \theta/2 + \alpha^2}{\sin^2 \theta/2 + 4\alpha^2} \left. \right\} \cos Dr_0 + \frac{h}{2\pi m_0 v a \sin \theta/2} \\
 & \times \left\{ \left(1 - \frac{r_0}{a} + \frac{\sin^2 \theta/2 - \alpha^2}{2(\sin^2 \theta/2 + \alpha^2)}\right) + \frac{2e^2 Z^*}{m_0 c^2 a} \right. \\
 & \times \left(1 - \frac{v^2}{c^2}\right)^{\frac{1}{2}} e^{-Cr_0} \left(1 - \frac{r_0}{2a} + \frac{1}{8} \frac{\sin^2 \theta/2 - 4\alpha^2}{\sin^2 \theta/2 + 4\alpha^2}\right) \\
 & \times \frac{\sin^2 \theta/2 + \alpha^2}{\sin^2 \theta/2 + 4\alpha^2} \left. \right\} \sin Dr_0 \left. \right]^2. \quad \dots \quad (10)
 \end{aligned}$$

Thus we arrive at an expression for the intensity of scattering by taking into account the *excluded phase-space* of the scattered electron. Now in the case of the

lighter elements α , $\frac{r_0}{a}$, $Cr_0 \approx 10^{-2}$, and $\frac{e^2 Z^*}{m_0 c^2 a} \approx 10^{-28}$,

where order of r_0 is known from the dynamical formula, which will be given below. In the case when a Coulombian field is considered and when $r_0 = 0$ the expression (10) approximates to that given by Mott in the case of the fast electron; but for moderate velocity of the electron the expression (10) with approximations cited above becomes

$$|\chi_{1,1}|^2 = \frac{e^4 Z^2}{4m_0^2 v^4} \operatorname{cosec}^4 \frac{\theta}{2} \cdot \cos^2 Dr_0, \quad \dots \quad (11)$$

which reduces to Rutherford's formula when $r_0 = 0$. So the expression (11) may be considered as an extension of Rutherford's classical formula.

The next important step is to determine whether r_0 is constant or depends on the impinging velocity and the angle of scattering of the electron. Mukherjee⁽¹³⁾, in his paper, has noticed that r_0 depends both on velocity

and the angle of scattering. *The distance between the vertex and the first focus of the hyperbola traced out by the scattering electron has evidently the same meaning as r_0 .* With the help of geometry and classical mechanics it is given by

$$r_0 = \frac{e^2 Z^*}{m_0 v^2} \left(\operatorname{cosec} \frac{\theta}{2} - 1 \right). \quad . \quad . \quad . \quad (12)$$

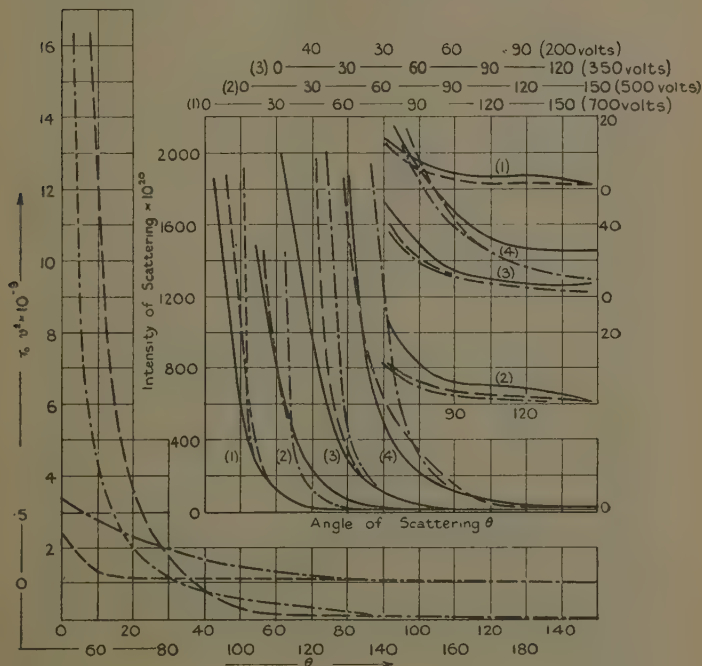
This dynamical expression shows the dependence of r_0 on v and θ ; but one is not justified in using the dynamical expression of r_0 in the wave statistical deduction of intensity. But it is all the more suggestive for the determination of the wave statistical value, which, it may be hoped, will be able to explain completely the fluctuating nature of the intensity distribution curve.

The experimental values of Hughes, McMillen, and Webb for the intensity of scattering by helium for 700, 500, 350, and 200 volts are compared graphically with the theoretical values calculated from (11). As the wave statistical value of r_0 is not at our disposal at present, we take the dynamical value of the same; we shall also take a set of empirical values. The variation of $r_0 v^2$ with the angle of scattering is represented by the curve with broken lines and dots and the empirical values by the broken line alone. The small flat curves in a portion of the figure represent the magnified values of the same at large angles. The dynamical value of r_0 depends inversely on the square of v , but the nature of dependence of the wave statistical value of r_0 on v is not known before we actually work it out. The curve representing the empirical values assumes the same nature of dependence on v as given by dynamical expression for r_0 . With these two sets of values for r_0 we calculate two sets of values of intensity from our scattering formula represented by eq. (11) with $Z^* = 27/32$ (He), and the values are compared with the experimental values represented graphically by the continuous curve. The flat short curves at the right side of the figure represents the values for large angles on a magnified scale.

It is found that the theoretical values calculated from the dynamical values of r_0 do not agree well with the

experimental values at small angles; but better agreement between theory and experiment is found with the empirical values of r_0 in the theoretical formula.

My best thanks are due to Prof. K. C. Kar, D.Sc., for taking interest in my present investigation.



References.

- (1) Rutherford, *Phil. Mag.* xxi. p. 669 (1911).
- (2) Born, *Z. f. Phys.* xxxviii. p. 803 (1926).
- (3) Oppenheimer, *Phys. Rev.* xxxii. p. 361 (1928).
- (4) Mott, *Proc. Roy. Soc. A*, cxxiv. p. 426 (1929); cxxvii. p. 658 (1930).
- (5) Dymond, *Proc. Roy. Soc. A*, cxxii. p. 571 (1929).
- (6) Bullard and Massey, *Proc. Camb. Phil. Soc.* xxvi. p. 556 (1930).
- (7) Arnot, *Proc. Roy. Soc. A*, cxxxiii. p. 615 (1931).
- (8) Faxen and Holtzmark, *Z. f. Phys.* xl. p. 307 (1927).
- (9) Allis and Morse, *Z. f. Phys.* lxx. p. 567 (1931).
- (10) MacDougall, *Proc. Roy. Soc. A*, cxxxvi. p. 547 (1932).
- (11) Massey and Mohr, "Theory of Atomic Collision," *Proc. Roy. Soc. A*, cxxxii. p. 605 (1931); cxxxvi. p. 289 (1932); cxxxix. p. 187 (1932); cxlvi. p. 880 (1934).

- (12) Hughes, McMillen and Webb, *Phys. Rev.* xli. p. 154 (1932).
 (13) Mukherjee, *Phys. Zeit.* xxxiv. p. 175 (1933); 'Current Science,'
 ii. p. 470 (1934).
 (14) Kar and Mukherjee, *Phil. Mag.* xvii. p. 993 (1934).

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XVI. *Theories of Ionization.* By J. S. E. TOWNSEND,
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1. **T**HE theory of ionization by collision in electrical discharges, which I gave many years ago, has been found to be in good agreement with the results of recent experiments with monatomic gases which have been made at the Electrical Laboratory, Oxford.

In this theory the coefficients of ionization of the electrons and positive ions are independent of the intensity of the current, and the ionization of the gas is attributed to single collisions of electrons and positive ions with molecules of the gas. The loss of energy of electrons in these collisions may be expressed as a potential, which is called the ionizing potential. There are also other collisions in which the electrons lose energy in amounts of the same order but less than the ionizing potential, and collisions in which the electrons lose only a very small part of their energy. A general theory of collisions, which is based on the results of various experiments, has also been developed in which the action of the electrons in different types of collisions with normal atoms is considered.

In the discharges which were investigated it was found that there was no loss of conductivity due to recombination of electrons with positive ions in the gas. Also in discharge-tubes there was no effect of recombination which contributed to an appreciable extent to the radiation from the uniform positive columns†. As in the case of ionization, the excitation both of the line spectrum and the continuous spectrum is attributed to single collisions of electrons with molecules of the gases.

* Communicated by the Author.

† 'Electricity in Gases,' pp. 405, 428, and 442.

In all cases where each electron collides with many molecules of a gas the energies of the electrons are distributed about a mean value and the interpretation of the experiments depends on the distribution about the mean.

This general theory provides a consistent explanation of the principal phenomena observed in numerous forms of electrical discharges.

2. Some physicists are more attracted by new theories of conductivity depending on the formation of metastable atoms. There are now at least two of these theories, one for pure and the other for impure gases, and the hypothesis which is common to both is that metastable atoms are formed in large numbers by the collisions of electrons with normal atoms. In each of these collisions the electron loses a definite amount of energy which is called the critical energy, and when the energy of an electron is slightly greater than the critical energy it makes very few elastic collisions before a collision occurs in which a metastable atom is formed.

This hypothesis is based principally on the results of experiments with impure monatomic gases, and the process of ionization which involves the action of metastable atoms on molecules of impurities is known as the "Stoss Zweiter Art."

The currents in which this action is said to have a preponderating effect are those in which the ratio of the electric force Z to the pressure p of the gas is of the order of the values of Z/p in the discharges between parallel plates when the pressure of the gas is greater than that corresponding to the minimum sparking potential. This theory forms the principal part of the new laws of collisions given by Franck and Hertz which are specially commended in papers published in the *Proceedings of the Royal Society*.

In view of the accounts of theories which are there given, it is necessary to state that the new laws of collisions are not accepted by many physicists who have made a careful study of the properties of currents in gases.

It is impossible to reconcile these laws of collisions with the properties of currents obtained under simple conditions. The phenomena observed in many experi-

ments depend on the distribution of the energies of electrons about a mean value, and no reliable conclusions can be deduced from the observations by calculations where statistical distributions are disregarded.

Also there are considerable errors in calculating the number of collisions of electrons with molecules when the free paths of electrons are taken to be the same as the free paths of small particles deduced from the theory of viscosity.

The process of ionization in a current depends on the probability of actions of various types, and it cannot be assumed that one type of collision is so probable that the number of collisions of other types becomes indefinitely small in ordinary discharges.

In the following discussion the different theories of the action of electrons in collisions with normal atoms are considered, and tested by comparing them with the principal properties of small currents obtained under simple conditions.

The smaller the currents the less the effects of double collisions of electrons with atoms in comparison with the effects of single collisions with normal atoms.

3. The investigations of the action of electrons in gases which have been made at the Electrical Laboratory, Oxford, include many experiments on the ionization of monatomic gases which had been carefully purified. The results are in complete agreement with the original theory of ionization by collision, and there was no evidence of any action by metastable atoms. In the paper on the ionization of pure neon* it was stated that the large increases in photo-electric currents in monatomic gases due to small quantities of impurities may also be explained by the original theory of ionization. The increase in conductivity may, in fact, be attributed to the collisions of electrons with molecules of the impurity.

This explanation depends on the number of collisions of electrons with molecules of impurities, and it may be described and examined more fully in connexion with the recent experiments of MacCallum and Klatzow on

* J. S. E. Townsend and S. P. MacCallum, *Phil. Mag.* vi. p. 857 (Nov. 1928).

the ionization in a mixture of helium with small measured quantities of argon.

4. In order to estimate the effects of collisions of electrons with molecules of a gas, it is necessary to consider the velocity of agitation of the electrons and the velocity in the direction of the electric force, since the number of collisions in a given volume depends on the ratio of these velocities. This number also depends on the mean free path of an electron between collisions with molecules of the gas, and the mean free path as found experimentally depends on the specification of a collision *. Most of the investigations show that, whatever definition of a collision be adopted, there are large differences in the mean free paths depending on the kinetic energy of the electrons.

5. The nature of the collisions of electrons with molecules of a gas when the energies of the electrons are small compared with the energy required to ionize the molecules, has been deduced from the investigations of the motion of electrons in gases which have been made at the Electrical Laboratory, Oxford. In these investigations the mean energy of agitation of the electrons and the mean velocity in the direction of the electric force were determined experimentally. It was found that when electrons move under a uniform electric force Z in a gas, a steady state of motion is attained in which the mean kinetic energy $m\bar{u}^2/2$ of the electrons and the mean velocity \bar{W} in the direction of the electric force depend only on the ratio of the force Z to the pressure p of the gas †.

The motion of the electrons resembles in many respects that which would be obtained if the collisions of the electrons with molecules of the gas were the same as the collisions of small particles of the same mass as an electron with elastic spheres of the same mass as a molecule.

In these collisions all directions of motion of a particle after a collision are equally probable, and the mean loss

* 'Electricity in Gases,' p. 293.

† J. S. E. Townsend, Proc. Roy. Soc. A, lxxxi. p. 464 (1908).
J. S. E. Townsend and H. T. Tizard, Proc. Roy. Soc. A, lxxxviii.
p. 336 (1913).

of energy of a particle in a collision is small; depending on the elasticity.

The experiments may, therefore, be interpreted by comparing the results with formulæ derived by the kinetic theory on the hypothesis that the collisions of electrons with molecules are the same as the collisions of small unchanged particles with elastic spheres.

With this specification of a collision, the mean free path l of an electron between collisions and the mean loss of energy $\lambda \cdot m\bar{u}^2/2$ of an electron in a collision, are obtained from formulæ which give l and λ in terms of the electric force Z , and the velocities \bar{u} and \bar{W} which are found experimentally.

6. In the following calculations the mean free paths thus obtained will be denoted by the letter l and L the corresponding free path at unit pressure ($L=lp$). The mean free paths terminated by collisions of other types will be denoted by suffixes.

The mean free path depends on the energy of the electron, and from the value of L corresponding to a given value of the energy $mu^2/2$, the number of elastic collisions of an electron with molecules of the gas in a given space may be determined by a simple formula. (It will be observed that the same formula does not give the number of collisions of other types, such as those in which there is a large loss of energy and radiation is excited or an atom is ionized.)

7. An equation has also been given by Pidduck * for the coefficient of elasticity of the molecules in terms of the velocities u and \bar{W} , the first estimate of the coefficient of elasticity for collisions of electrons being that which was obtained for air.

It was thus found that the coefficient was nearly the same as the value corresponding to perfect elasticity when the energies of the electrons were of the order of one volt.

For some gases the coefficient of elasticity f is almost exactly the same as the value $f=1$ corresponding to perfect elasticity. For electrons with energies of about one half a volt, the values of f are .9990 for air, .9990 for hydrogen, .9998 for nitrogen, 1.00001 for helium.

* F. B. Pidduck, Proc. Roy. Soc. A, lxxxviii. p. 296 (1913).

These collisions, in which the coefficient of elasticity has been found to be near the value $f=1$, may be referred to as elastic collisions.

8. The mean free path L of the electrons in argon, helium, and hydrogen at one millimetre pressure*, corresponding to the different values of the mean energy of agitation \bar{E} of the electrons, are given in Table I., also the coefficient λ for helium and hydrogen. The energy E is given as a potential in volts ($m\bar{u}^2/2 = \bar{E}e/300$, e being the atomic charge).

The value of λ in argon was not determined for values of \bar{E} less than 4.4 volts. With this energy the value of λ was 1.64×10^{-5} .

TABLE I.

E.	.15	.37.	.59.	1.85.	3.7.	5.2.
$L \times 10^{-2} \begin{cases} \text{A} \\ \text{He} \\ \text{H}_2 \end{cases}$	113	161	138	29.5	13.6	10.4
	6.5	5.4	5.1	4.8	5.2	5.5
	3.4	2.8	2.35	2.1	3.0	4.0
$\lambda \times 10^{-4} \begin{cases} \text{He} \\ \text{H}_2 \end{cases}$	2.3	2.5	2.4	2.4	2.85	4.2
	27	29	35	71	217	480

In helium the mean energies of 1.85, 3.7, and 5.2 volts are obtained with the values of Z/p .95, 1.9, and 3.1, respectively. Thus in helium the mean energy \bar{E} in volts is approximately $2 \cdot Z/p$ for values of Z/p from .5 to 2. For larger values of Z/p the change in \bar{E} with Z/p diminishes gradually.

9. In argon the energy \bar{E} is much greater than in other gases for small values of Z/p . Also, there is an abrupt change in the rate of increase of \bar{E} with Z/p . The mean energy \bar{E} increases rapidly, as the ratio Z/p is increased from the small value (.2), where \bar{E} is 4.4 volts, to the value $Z/p=1$, where \bar{E} is 10.8 volts. About this point the rate of increase of \bar{E} with Z/p changes abruptly and becomes very small, the value of \bar{E} being 12 volts when Z/p is 15. This result has been interpreted as showing

* J. S. E. Townsend and V. A. Bailey, Phil. Mag. xlii. (1921); xliii. and xlv. (1922); and xlvi. (1923).

that with energies of about 12 volts a large number of the free paths of the electrons are terminated by collisions in which the electrons lose large amounts of energy.

The abrupt increase in the number of these collisions which occurs in argon as the energy \bar{E} increases is partly due to the fact that the energies of the electrons are not widely distributed about the mean value \bar{E} as in other gases. It will also be seen from other experiments that the free paths of electrons with energies of about 15 volts, which are terminated by collisions in which there are large losses of energy, are very much shorter than the free paths of electrons with energies of about 5 volts.

10. It is of importance to observe that none of the free paths L given in Table I. are the same as the mean free paths of small particles obtained from the viscosity of the gas. Taking the mean free paths of molecules given in Kaye and Laby's Tables, the mean free paths of small particles moving with large velocities are found to be 4.3×10^{-2} cm. in argon at one millimetre pressure, 12.2×10^{-2} cm. in helium, and 8.7×10^{-2} cm. in hydrogen. Thus for values of \bar{E} from 1.5 to 5.2 volts the mean free paths of electrons in argon are much longer and those in helium and hydrogen much shorter than the mean free paths of small particles deduced from the viscosity.

There is a considerable agreement between the values of L deduced from the velocities \bar{u} and \bar{W} and the free paths found by Ramsauer's method, as far as the change of free path with the energy is concerned. The two methods of investigation are quite different, and there is also a difference in the definition of a collision, so that exact agreement cannot be expected. Ramsauer's method is the more suitable for measuring free paths of electrons with energies of the order of 20 volts, which include paths that are terminated by collisions in which the loss of energy of the electrons may be either large or small. These free paths are of interest in considering the results of experiments on the ionization of argon.

The mean free paths L_R in argon * found by Ramsauer's method for electrons with energies for 9 to 20 volts are given in Table II., and those for helium † in Table III. The energies E are given in volts.

* C. Ramsauer, *Ann. d. Phys.* lxxii. p. 351 (1923).

† C. Ramsauer and R. Kollath, *Ann. d. Phys.* (5), xii. p. 529 (1932).

11. In the steady motion of electrons in a uniform electric field the energies of the electrons are distributed about the mean energy $m\bar{u}^2/2$ even when the losses of energy in the collisions are very small. The distribution about the mean is not the same in all gases, as it depends on the variation of the mean free path L with the energy. In argon, where the mean free path diminishes as E increases, the distribution is not so wide as in helium, where there is a small increase in L as E increases. So that in helium the number of electrons with energies four or five times the mean energy is much greater than in argon.

The difference between the two gases in this respect is shown by experiments on the determination of the force in the positive columns of discharge-tubes.

TABLE II.

Argon.

E.	$100 \times L_R$ cm.
9	1.6
12	1.25
16	1.4
25	2.0

TABLE III.

Helium.

E.	$100 \times L_R$ cm.
5.3	5.2
10.7	6.7
15.8	8.3
19.2	9.0

In a tube 2.6 centimetres in diameter containing pure helium at 10 millimetres pressure the force in the positive column is 19 volts per centimetre, so that the ratio Z/p is 1.9, and the mean energy of agitation of the electrons is 3.8 volts. This shows that some of the electrons acquire energies about six times the mean energy which is required to excite the line spectrum and to ionize the gas. As the rate of ionization which is necessary to maintain the current is very small, only a small proportion of the total number of the electrons in a given space have these large energies*.

A satisfactory explanation of the conductivity and radiation from the gas is thus obtained on the hypothesis that the ionization and radiation are due to single collisions of electrons with normal atoms of the gas.

* Phil. Mag. ix. p. 1145 (June 1930); xi. p. 1113 (May 1931); xvi. p. 729 (1933).

This theory is in agreement with the experiments which show that with small currents the electric force in the positive column is a constant independent of the intensity of the current, and, consequently, the number of collisions in which atoms are ionized and the number in which radiation is excited are proportional to the current *.

12. According to the new theories the energy required to form a metastable atom in helium is 19.77 volts, which is less than the energy required to excite radiation or to ionize atoms of the gas. The ionizing potential is generally accepted as being 24.5 volts.

The potential 19.77 is a critical potential such that an electron with energy slightly exceeding this value cannot make many elastic collisions before a collision occurs in which the electron loses its energy and converts the normal atom into a metastable atom.

The probability of an electron making a collision of this type before it attains sufficient energy to ionize the gas increases as the ratio of Z/p , diminishes, and in the positive columns of discharges where the ratio Z/p is very small, no appreciable number of electrons would attain energies sufficient to ionize normal atoms of the gas, or to excite radiation.

In order to avoid this difficulty, it is stated that radiation is excited and ionization is obtained by the collisions of electrons with energies of about 4 or 5 volts with metastable atoms. Thus two collisions with the same atom would be required to excite radiation or to ionize an atom of the gas, and with small currents both the intensity of the radiation and the rate of ionization would be proportional to the square of the current.

This is not in accordance with the properties of currents of the order of one milliamperere in discharge-tubes. With these small currents it has been found that the intensity of the radiation from the positive column is proportional to the current and the force is independent of the current.

In order to account for these observations it would be necessary to introduce an additional hypothesis with regard to the length of time a metastable atom may exist

* J. S. E. Townsend and F. Ll. Jones, *Phil. Mag.* xii. (Oct. 1931); J. S. E. Townsend and M. H. Pakkala, *Phil. Mag.* xv. (Sept. 1932); J. E. Keyston, *Phil. Mag.* xv. p. 1162 (June 1933).

in the gas before returning to the normal state, but it would be difficult to obtain an approximate agreement with the experiments.

Thus the new theories do not afford a satisfactory explanation of the properties of the uniform positive columns of discharges in wide tubes. But a much more definite test of the theories is obtained by considering the properties of small currents of the order of one micro-ampere between parallel plate electrodes.

13. The new theories were at first proposed in order to explain the ionization in very small currents where the ratio Z/p is greater than in the uniform positive columns of discharges in wide tubes, and the total loss of energy of the electrons in elastic collisions is small compared with other losses.

It is, therefore, of interest to consider experiments with small currents in pure and impure gases, where the ratio Z/p is of the order of 20.

The ionization of neon and helium under these conditions has been deduced from measurements of the photo-electric currents in the gases which had been carefully purified *.

The apparatus used in these experiments was contained in a quartz envelope and was heated to a high temperature in order to expel occluded gases.

The electrodes were parallel plates of nickel, arranged so that the distance z between the plates could be adjusted from 1 millimetre to 12 millimetres by means of a micrometer screw.

A number n_0 of electrons was set free from the negative electrode by ultra-violet light, and moved under a uniform force Z to the positive electrode at the potential Z/z , the negative electrode being at zero potential.

In the experiments with helium the ratio Z/p ranged from 6 to 180.

The currents were measured with the plates at different distances apart z , so that the electrons moved under the same electric force Z to the positive electrode at the potentials Z/z . With potentials less than 20 volts the number of electrons n received by the positive electrode

* J. S. E. Townsend and S. P. McCallum, *Phil. Mag.* vi. p. 857 (Nov. 1928); xvii. p. 678 (1934). The coefficients of ionization obtained in the earlier experiments are inaccurate, as the impurities were not completely removed.

was equal to n_0 , but for larger potentials n increases with the potential. The increase in the current with the potential is gradual, and it is impossible to assign a definite value to the minimum potential at which the number n exceeds n_0 .

With a given force Z . and distance z between the plates, the current depends on the pressure p of the gas, and is a maximum for a certain pressure which is proportional to Z .

In helium the maximum currents are obtained when the ratio Z/p is about 40, but at this point the rate of change of the current with the pressure is small.

The photo-electric currents n obtained in pure helium at 2 millimetres pressure, with a force of 100 volts per centimetre, are given in arbitrary units by curve 1 in the figure. The ordinates are proportional to n , the current n_0 obtained with potentials less than 20 being taken as 100. The abscissæ are the potentials $Z \cdot z$ in volts. The values of n/n_0 given by this curve are approximately the maximum values of the ratio n/n_0 , which can be obtained with a potential $V=Z \cdot z$ in pure helium.

14. In order to form a consistent theory of the conductivity it is necessary to take into consideration the following general properties of the photo-electric currents.

When the electric force Z and the gas-pressure p are constant, the ratio n/n_0 for any distance between the electrodes remains constant when the number n_0 of the electrons set free from the negative electrode by the ultra-violet light is increased or diminished by changing the intensity of the light.

In these experiments the currents were found by measuring the electro-static charge received by the negative electrode, while the light acted for 10 or 20 seconds

With the smaller currents, which were of the order of 5×10^{-13} ampere, the total number of electrons that pass between the plates is comparatively small.

Even if each electron formed a metastable atom when the potential $Z \cdot z$ is about 40 volts, and each metastable atom remained in the gas during the time of an experiment, the total number of metastable atoms would be very small and the number of collisions between electrons and metastable atoms would be negligible.

15. The ionization of the gas and the radiation from the current must therefore be attributed to single collisions of electrons with atoms of the gas. This applies to large photo-electric currents as well as to small currents, since the ratio n/n_0 is independent of the current. With larger distances between the electrodes, where the action of positive ions becomes effective the coefficients of ionization α and β of the electrons and positive ions remain constant, as the distance Z between the electrodes is increased to the value d where $Z.d$ is the sparking potential.

Also with the electrodes at the distance apart d , the potential required to maintain a continuous current of about one to ten micro-amperes is exactly the same as the sparking potential $Z.d$. If there were any additional process of ionization in the continuous currents the conductivity would be increased and the potential required to maintain the currents would be less than $Z.d$. The experiments therefore show that the process of ionization and all other actions of electrons in collisions in these currents are the same as in the small photo-electric currents.

The radiation from the continuous currents maintained by the potential $Z.d$ is easily observed, and the lines of the helium spectrum may be seen by a small direct vision spectrocope. It must, therefore, be concluded that similar radiation of very small intensity is also excited in the small photo-electric currents by single collisions of electrons with atoms of helium.

It is necessary to take into consideration these properties of currents between parallel-plate electrodes in order to test the validity of the theories of ionization which depends on the action of metastable atoms.

16. The "Stoss Zweiter Art" theory is fully described by Atkinson * in the Proceedings of the Royal Society, and is given as an explanation of the relation of the current to the potential obtained in experiments on thermionic currents in helium and in neon, where large increases were observed in the currents with potentials less than 25 volts in helium and less than 21 volts in neon.

The metastable atoms are formed by single collisions of electrons with normal atoms. In currents in helium

* R. d'E. Atkinson, Proc. Roy. Soc. A, cxix. p. 325 (1928).

where the pressure p is of the order $Z/20$ or $Z/40$, the number of collisions of other types where the electrons may lose large amounts of energy is not appreciable.

The energy of an electron required to form a metastable atom in helium is 19.77, which is less than the energy required to excite radiation or to ionize normal atoms of the gas. As the ratio Z/p diminishes the number of collisions in which metastable atoms are formed increases in comparison with the number of collisions in which the electrons have sufficient energy to excite radiation or to ionize atoms of helium.

Thus in the currents maintained by the sparking potentials $Z.d$, with the gas at pressures greater than $Z/20$, there would be no appreciable ionization of helium atoms and no lines of appreciable intensity in the helium spectrum due to single collisions of electrons with normal atoms.

17. The metastable atoms diffuse slowly throughout the space between the electrodes and collide with molecules of impurities, with the result that radiation is excited in some of these collisions and in others the molecules of the impurities are ionized. This action is known as the "Stoss Zweiter Art."

Since the ratio of the number of collisions of metastable atoms in which radiation is excited to the number in which molecules are ionized does not depend either on the pressure of the helium or the amount of the impurity, it must follow that any change in the intensity of the radiation (due to a change in the number of metastable atoms) is accompanied by a proportional change in the ionization of the gas.

The metastable atoms also have the property of setting free electrons from the negative electrode which contribute to the conductivity of the gas, but there seems to be a difference of opinion among the advocates of new theories as to the importance of this action.

18. In the first form of the new theory it is supposed that there is always a small amount of impurity in helium, and the large increases in the photo-electric currents obtained by increasing the potential between the electrodes are attributed to the "Stoss Zweiter Art" action. In this theory only the line spectrum of the impurity would be

observed in the radiation from the current, which is excited by metastable atoms in collisions with molecules of impurities.

It is, however, by no means difficult to remove impurities to such an extent that the radiation from the current is free from any lines due to impurities, and it is unreasonable to suppose that under these conditions the ionization is due to the "Stoss Zweiter Art" action to any large extent.

It remains, therefore, to consider the form of the new theory in which the increases in the photo-electric currents are attributed to electrons set free from the negative electrode by the action of metastable atoms. In this case there would be no appreciable radiation in the visible spectrum, also there would be no positive ions in the gas, so that this form of the new theory is even more unreasonable than the first.

Thus, in neither form of the new theories is there any explanation of the fact that the helium lines, and only the helium lines, are observed in the spectrum of the radiation from the current maintained in the space between parallel plates by the potential $Z \cdot d$, when the gas is purified by the ordinary methods.

19. The principal process of ionization, when the helium is impure, may be deduced from the photo-electric currents in helium, which have been determined by MacCallum and Klatzow with the apparatus contained in a quartz envelope. The experiments were made in order to compare the currents in pure helium, and in pure argon with the currents in a mixture of helium with small measured quantities of argon. The results of a set of their experiments * are given by the curves in the figure.

Each curve gives the photo-electric current n obtained with a force Z of 100 volts per centimetre in terms of the potential $Z \cdot z$ between the electrodes.

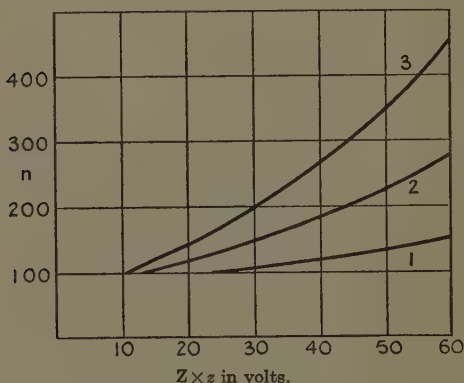
Curve 1, as already explained, gives the currents in pure helium at 2 millimetres pressure ($Z/p=50$), curve 2 the currents in pure argon at half a millimetre pressure ($Z/p=200$), and curve 3 the currents in a mixture of helium

* S. P. MacCallum and L. Klatzow, 'Nature,' cxxxi. p. 481 (June 10, 1933).

at 6.6 millimetres pressure and argon at .00165 mm., .025 per cent. of the helium ($Z/p=15$).

With these pressures the rate of increase of the current, with the distance between the plates, was about the maximum in each case.

It will be observed that with the mixture of helium and argon there is a considerable increase in the current between the plates with potentials much less than 19.77 volts. These increases cannot be attributed to metastable atoms of helium, as none of the electrons acquire sufficient energy to form metastable atoms. The experiments also cast a doubt on the accuracy



with which critical potentials have been determined for monatomic gases.

In argon the first critical potential is said to be 12 volts, and the ionizing potential 16 volts; but it is clearly shown by curve 3 that there is an increase in the current when the potential is less than 16 volts. It would also be difficult to explain the large currents obtained with distances from 2 to 3 millimetres between the plates if the ionizing potential were 16 volts.

20. These experiments provide the data required to calculate the lengths of the free paths, which are terminated by the collisions in which atoms of argon are ionized. The results are of considerable importance, as they show that these free paths are much shorter than

the free paths obtained from the viscosity of argon and helium.

In order to measure the free paths it is necessary to find the number of collisions in which the electrons lose energy in large amounts.

In addition to the collisions in which atoms of argon are ionized, the electrons also lose energy in large amounts in some of the collisions with atoms of argon and of helium which are not ionized.

Let N_1 be the number of atoms of argon which are ionized in the space between two planes at distances z_1 and z_2 from the negative electrode, C_1 the loss of energy in each of these collisions, N_2 the number of collisions in the same space with atoms that are not ionized, in which the electrons lose energy in large amounts. It may be assumed that the number N_2 is made up principally of the number of collisions with atoms of argon which excite radiation, and that the mean loss of energy C_2 in these collisions is about 12 volts.

In the steady state, where the coefficient of ionization is constant, the mean energy \bar{E} of the electrons is the same at the planes z_1 and z_2 , and the following relation * is obtained between the energies :

$$N_1 C_1 + N_2 C_2 + N_1 \bar{E} = N_1 (Z/\alpha - G_1). \quad (1)$$

In this case α is 3.0, the potential Z/α is 33 volts, and G_1 is a small correction of about 2 volts, to allow for the loss of energy of the electrons in elastic collisions with atoms of helium.

21. Another relation between the energies is obtained from curve 3, since the area of the curve $\int_0^{z_1} nZ dz$ is the total energy H acquired by all the electrons in moving under the action of the force Z to a plane at a distance z_1 from the negative electrode. This applies to the shorter distances z_1 where the action of the positive ions may be neglected, and the increase in n with the distance z is due to ionization by the collisions of electrons with atoms of the gas. At the distance of 3.1 millimetres from the negative electrode, H is $41 \times n_0$, n is $2n_0$, and the electrons arrive at the plane $z_1 = 31$ with the energy

* *Phil. Mag.* xiv. p. 1071 (1923).

$2n_0\bar{E}$. In traversing the gas the energy lost by ionization is n_0C_1 , and the amount lost in the collisions that excite radiation is $n_0N_2C_2/N_1$. The following relation between the energies is therefore obtained :—

$$n_0C_1 + n_0N_2C_2/N_1 + 2n_0\bar{E} = 41 \times n_0 - G_2, \quad (2)$$

G_2 being a small correction involving the loss of energy of electrons in elastic collisions and the energy of the electrons at the negative electrode. The value of $(N_1C_1 + N_2C_2)$ obtained by eliminating \bar{E} from equations (1) and (2) is approximately $20 \times N_1$. Thus if C_1 be 14 volts and C_2 12 volts, the number N_2 is approximately $\cdot 5 \times N_1$.

22. In order to estimate the probability of a collision in which an atom of argon is ionized, it is necessary to find the number of electrons with energies greater than the ionizing potential at distances of about 2 millimetres from the negative electrode, when the electrodes are 2.6 millimetres apart.

These electrons will be referred to as the group [S] to distinguish them from the electrons with energies less than 14 volts. At distances z , less than 2.6 millimetres, there is no appreciable effect of positive ions, and the only electrons in the group [S] are electrons which were set free from the negative electrode, and did not excite radiation or ionize atoms of argon in collisions at distances less than z from the negative electrode.

The number of atoms that are ionized at distances less than z from the negative electrode is $(n - n_0)$ when the positive electrode is at the distance z , and for an approximate calculation the number of atoms ionized in the space between two planes at distances z_1 and z_2 from the negative electrode may be taken to be the difference between the currents corresponding to those distances as given by curve 3 in the figure. The number of electrons that lose energy in the large amounts C_1 and C_2 , at distances less than z from the negative electrodes, is $1.5(n - n_0)$, and the number in the group [S] at the distance z is $(n_1 - 1.5(n - n_0))$.

Let $hSdz$ be the number dn of atoms ionized in the space between the two planes at distances z and $z + dz$ from the negative electrode.

The coefficient h is given by the equation

$$dn/dz = h(2.5n_0 - 1.5n), \quad \dots \quad (3)$$

the values of dn/dz and n being given by curve 3 in the figure.

At the distance 2 mm. from the negative electrode, the current n is $1.45 \times n_0$ and dn/dz is $4.4 \times n_0$, and the value of h for the group [S] at the distance 2 mm. from the negative electrode is 13.5. The mean loss of energy of these electrons in elastic collisions with atoms of helium is about 1.5 volt, so that the energy of the group at 2 mm. from the negative electrode is about 18.5 volts.

The coefficient h diminishes with the energy of the electrons and is about 8 for electrons with energies of 16 volts.

23. If U be the velocity of agitation and W the mean velocity of the group [S] in the direction of the electric force, the total length of the paths of these electrons in the space between two planes at a distance apart dz is $SU dz/W$. The mean free path for any type of collision may be defined as the ratio of the total length of the paths to the number of collisions of that type. Thus the mean length l_1 of the paths terminated by collisions in which atoms of argon are ionized is U/Wh .

If p_1 be the pressure of the argon, the mean free path L_1 for these collisions with the argon at one millimetre pressure is $l_1 p_1$. The relation between L_1 and h is therefore given by the equation $h = Up_1/WL_1$.

The velocity W of the group [S] depends on all the collisions of electrons with atoms of the gas, but in the mixture of helium and argon the partial pressure p_1 of the argon is so small that it may be neglected, and the velocity W is determined by the pressure p of the helium.

Since the electrons in the group [S] have approximately the same energy E , the velocity W is $2ZeL/3mUp$, and the ratio U/W is $3Ep/ZL$, L being the mean free path of electrons in elastic collisions with atoms of helium at one millimetre pressure. The equation for h thus becomes

$$h = 3Epp_1/ZL_1L, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and from this equation the product $L \cdot L_1$ is obtained.

24. In the mixture of helium at 6.6 millimetres pressure with argon at 1.65×10^{-3} mm. pressure, the value of h for electrons with the energy E of 18.5 volts is 13.5, and from the above equation the product $L \cdot L_1$ is found to be 4.7×10^{-4} cm.².

This number is less than one-tenth of the product of the mean free paths 12.2×10^{-2} cm. and 4.3×10^{-2} cm. of small particles in helium and argon, as deduced from the viscosity of the gases. The effect of the argon regarded as an impurity would be greatly underestimated by taking the latter as the free paths of the electrons.

It appears from the mean free paths given in Tables I. and III. that the mean free path L for elastic collisions in helium of electrons with energies of 18.5 volts cannot be less than 5.5×10^{-2} cm., and it must be concluded that in argon the electrons with this amount of energy have very short free paths ($L_1 = 9 \times 10^{-3}$), which are terminated by collisions in which there is a large loss of energy. There is, therefore, a remarkable difference between the mean free path L of electrons in argon, with energies of .4 volt, terminated by elastic collisions and the mean free path L_1 of electrons with energies of 18.5 volts terminated by collisions in which atoms are ionized, the free path L being $180 \times L_1$.

25. Owing to the uncertainty of the lengths, or the number of free paths terminated by elastic collisions in pure argon for electrons with energies of 15 to 20 volts, the mean free path L_1 cannot be determined from the experiments with pure argon, but the ratio N_2/N_1 may be found from equations 1 and 2, which do not depend on the lengths of the free paths.

The value of α for pure argon as given by curve 2 is 2.1, and the ratio N_2/N_1 is 2, assuming C_1 to be 14 volts and C_2 to be 12 volts. Thus the number of collisions in which radiation is excited is twice the number in which the atoms are ionized.

26. The changes in the ionization of the mixture of helium and argon due to changes in the pressures of the gases may be explained as follows :—

With a given force Z and pressure p of the helium, the ratio N_2/N_1 diminishes and the mean energy \bar{E} increases as the pressure p' of the argon is reduced. At a certain pressure P' the number N_1 of the atoms ionized in the space between two planes, z_2 and z_1 , is a maximum, and at this pressure the quantity $(N_2 C_2 + N_1 \bar{E})$ in equation 1 is a minimum. With the force of 100 volts per centimetre, and the helium at 6.6 millimetres pressure, the maximum

current n at distances from 1.5 to 2.5 millimetres from the negative electrode is obtained with the argon at a pressure of about 1.65×10^{-3} mm.

The ionization of the gas at these distances from the negative electrode, which would be obtained with smaller amounts of argon, may be deduced from the values given by curve 3 in the figure.

The photo-electric currents with the argon at different pressures are easily obtained by integrating equation 3, since the value of h is proportional to the pressure of the argon, and the integral $\int_0^z h dz$ is given by curve 3 for the pressure 1.65×10^{-3} mm. It is thus found that if the pressure of the argon be reduced from 1.65×10^{-3} to $2 \cdot 10^{-4}$ mm., the current n at 1.5 millimetres from the negative electrode is reduced from $1.2 \times n_0$ to $1.02 \times n_0$, and the current at 2.4 millimetres from the electrode is reduced from $1.6 \times n_0$ to $1.16 \times n_0$.

For pressures less than 2×10^{-4} mm. the values of $(n - n_0)$ at distances less than 2.5 mm. from the negative electrode are proportional to the pressure.

27. The changes in the ionization, due to changes in the pressure of the helium, may also be explained by this theory. The ionization, with the helium at pressures p greater than 6.6 millimetres may be considered, taking the force to be 100 volts per centimetre and the argon at a small pressure p' . As before, the ratio N_2/N_1 increases, as the pressure p of the helium is increased.

The increases in the pressure of the helium also give rise to large reductions in the energy \bar{E} of the electrons [S] at a distance z from the negative electrode, due to losses of energy in elastic collisions with atoms of helium. These losses are most noticeable with the larger energies, as is shown by a simple calculation.

The mean loss of energy of the electrons in the group [S] with energy E in traversing a small distance $(z_2 - z_1)$ between the two planes parallel to the electrodes under the action of the force Z is $3\lambda \cdot E^2 p^2 (z_2 - z_1) / ZL^2$, p being the pressure of the helium and L the mean free path for elastic collisions in helium at one millimetre pressure. The loss of energy increases in proportion

to E^2 , and for a certain energy E_1 , the mean loss of energy in elastic collisions is equal to the energy $Z \times (z_2 - z_1)$ gained in moving through the distance $(z_2 - z_1)$ in the direction of the force ($E_1 = ZL/p\sqrt{3\lambda}$). Taking the mean free path to be 7×10^{-2} cm., the value of E_1 is 20 volts when Z/p is 8 ($Z = 100$ volts per cm. and $p = 12.5$ mm.).

With these values of Z and p the rate of increase dE/dz of the energy of the group [S] is much less than Z .

If the energy of a group of electrons at the plane z_1 parallel to the negative electrode be 15 volts, the distance between this plane and the plane z_2 , where the mean energy is 18 volts, is .75 mm. (when $Z = 100$ and $p = 12.5$).

Thus in passing from the plane z_1 , where the mean energy of the electrons is 15 volts, to the plane z_2 , where the mean energy is 18 volts, the average number of collisions of electrons with atoms of helium is increased by the factor of 9, and the probability of a collision of an electron with an atom of argon at a given pressure p , is increased by the factor 5, when the pressure of the helium is increased from 6.6 to 12.5 mm.

Thus the process of ionization of the argon by collisions of electrons with energies less than 19.77 volts would be approximately the same in a mixture of helium at 12.5 mm. and argon at 3.3×10^{-4} mm. pressure, as in the mixture of helium at 6.6 mm. pressure with argon at 1.65×10^{-3} mm. pressure. In the former case the amount of the argon is 2.6×10^{-3} per cent. of the helium, and in the latter case the amount is 2.5×10^{-2} per cent.

The original theory of ionization therefore provides an adequate explanation of the large increases in conductivity which are obtained with small percentages of argon under the above conditions. If there are other processes of ionization their effects are small compared with the ionization by single collisions of electrons with atoms of argon.

With the helium containing argon or other impurities in amounts smaller than those considered above, a larger proportion of the electrons acquire sufficient energy to excite the helium spectrum or to ionize helium atoms. The energy required to excite the bright yellow or green helium lines is about 23 volts and these lines become much stronger than the lines due to impurities as the amount of the impurities diminish. But the electrons with energies of 20 volts, collide with large numbers of

helium atoms before they acquire sufficient energy to excite the yellow or green lines, so that it is necessary to suppose that the probability of an electron losing a large amount of energy in one of these collisions is very small.

Thus the hypothesis with regard to the formation of metastable atoms involved in the new theory of collisions is inconsistent with the fact that the lines of the helium spectrum become more prominent as the amount of the impurity is reduced.

XVII. *Note on Cosmic Ray Ions and the Shower producing Radiation.* By F. H. NEWMAN, D.Sc., F.Inst.P., Professor of Physics, and H. J. WALKER, M.Sc., A.Inst.P., Demonstrator in Physics, Washington Singer Laboratories, University College, Exeter *.

ONE of the most striking features of the formation of secondary particles as a result of interactions between cosmic radiation and atoms is what is known as the "shower phenomenon." These showers are observed in stereoscopic photographs obtained with counter-controlled Wilson expansion chambers as multiple tracks diverging downwards mainly from some region in the material surrounding the chamber. The secondary particles originate in numerous groups, following probably, on encounters with atomic nuclei. It appears, however, that a shower is not formed by a single process, but by several successive processes, for all the secondary particles do not diverge from a common centre. Among these particles negative and positive electrons are found in approximately equal numbers, which suggests that the phenomenon of materialization of energy plays an important part in the production of showers, and since hard γ -rays are known to be absorbed mainly by the production of positron-negatron pairs, it is possible to identify the shower producing radiation with photons of high energy. It is significant, as Blackett† has pointed out, that the absorption coefficient of γ -rays of

* Communicated by the Authors.

† Blackett, International Conference on Physics, London, 1934.

$2-5 \times 10^6$ e.v. energy is numerically nearly the same, and varies in the same way with atomic number of the absorber as does the shower producing radiation.

The identification of the shower producing radiation with photons is confirmed by the photographs of Anderson, Millikan, Neddermeyer and Pickering*, which have revealed many examples showing that incident non-ionizing rays were absorbed by electron shower formation in plates of lead placed in the expansion chamber. These photographs have afforded strong evidence that the non-ionizing rays were to be identified with photons, many of which were proved to be of secondary origin.

In addition it is to be noted that the cosmic particles observed at sea-level, or on mountains, are divided into two sharply separated groups; a soft group for which the mean penetrating power is equivalent to several centimetres of lead, and a hard group for which the mean penetrating power is several metres of lead.

It has never been possible to show the formation of the hard group of particles in matter, and this suggests that they are not produced in the atmosphere by non-ionizing primary radiation, but that they belong to the primary radiation itself. This point of view has been confirmed by the recent experiments which have demonstrated the existence of the latitude and azimuthal effects, since the particles which are deflected by the earth's magnetic field belong to the hard group, as is shown by the fact that the azimuthal dissymmetry gets greater if the particles of lowest energy are filtered out.

The connexion between the shower producing radiation and the soft group of particles is clear; the latter are, in fact, secondary electrons arising from the showers. But the natural hypothesis of identifying the shower producing radiation with the hard group of primary cosmic particles does not suffice to explain the observed facts, since the shower producing radiation has altogether different properties from the corpuscular radiation. The form of the absorption curve for the shower producing radiation obtained at sea-level suggests that this radiation is not identical with the primary radiation, but that it is a secondary radiation due to the hard cosmic particles. It therefore appears probable that the bulk of the secondary

* Anderson, Millikan, Neddermeyer and Pickering, *Phys. Rev.* **xlv.** p. 352 (1934).

cosmic ray electrons arise through the absorption of photon intermediary rays, which are produced in radiative impacts by the incoming primary corpuscles.

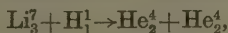
In this connexion some recent experiments of Lea* are of significance.

Lea has bombarded hydrogen, carbon, aluminium, sulphur, nickel, copper, zinc, silver, mercury, lead, and bismuth with the neutrons of Po-Be, and in a few cases with the neutrons of smaller average energy from Po-B. In all cases γ -rays were observed, and although it is known that many of these nuclei undergo capture disintegration (and it has been proved that γ -rays are often emitted in such transformations), the order of magnitude of the present effect is considerably greater than can be allowed for disintegration phenomena of the types previously studied.

However, it is possible that nuclear transformations occur, whereby the nuclei or the bombarding particles are raised to states of higher energy at the expense of the energy of motion of the particle, but no synthesis takes place. Subsequently a quantum or quanta of radiation are emitted by the excited system. The results quoted suggest that this a frequent mode of interaction between neutrons and nuclei, and it is probable that as many as half of the close collisions between neutrons and heavy nuclei result in excitation without capture.

These results suggest that, if the primary cosmic rays are high speed ions, such as protons, they may interact with nuclei and cause excitation without capture taking place. Thus the shower producing radiation probably consists of nuclear γ -radiation due, either to excitation of nuclei in the atmosphere, or to the excitation of the incident particles themselves.

This is suggested by the recent work of Crane and Lauritsen†, who, on bombarding lithium with protons, obtained γ -rays of energy 12 m.e.v. and 4 m.e.v., which they believe constitute evidence for one, and possibly two, excitation levels in the α -particle. The 12 m.e.v. component must be ascribed to the action



because this appears to be the only reaction involving

* Chadwick and Feather, International Conference on Physics (1934).

† Crane and Lauritsen, International Conference on Physics (1934).

lithium and protons in which sufficient energy is released. That such high energy radiation could be emitted by the impact of the protons on the lithium nuclei seems very improbable, and presumably, therefore, the only possible source of the radiation is the final product He_2^4 . It is more difficult to account for the 4 m.e.v. quantum, but Crane and Lauritsen suggest it could be due to an additional level in the α -particle lying above the 12 m.e.v. level already discussed. The existence of this level would suggest the possibility of the emission of γ -radiation of energy 16 m.e.v. from an α -particle, due to the direct transition from the level 12 m.e.v. + 4 m.e.v. = 16 m.e.v. to the ground state.

As the experiments of Compton and Stephenson* suggest that there exists as a component of the primary cosmic rays a group of ions which are either neutral or with a ratio of charge to mass equal to, or greater than, that of the α -particle, we suggest that high speed heavy ions may be incident on the upper atmosphere. Thus the shower producing radiation may be due to excitation of the incoming ions by inelastic collisions with nuclei, and if some of these ions are α -particles, the radiation may have quantum energy of the order 12 or 16 m.e.v. Thus the shower producing radiation may be a secondary nuclear γ -radiation arising as a result of interaction (most probably by inelastic collisions) between the high speed ions forming the primary cosmic radiation and the nuclei of the elements in the atmosphere.

XVIII. *The Non-observance of Induced β -radioactivity with the Light Elements.* By H. J. WALKE, M.Sc., A.Inst.P., Demonstrator in Physics, Washington Singer Laboratories, University College, Exeter †.

ONE of the most significant facts emerging from the recent work on the production of β -radioactive isotopes by bombarding stable elements with neutrons is the failure to detect with certainty induced β -radioactivity among the light elements of atomic number less than that

* Compton and Stephenson, Phys. Rev. xlv. p. 441 (1934).

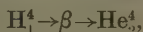
† Communicated by Prof. F. H. Newman, D.Sc.

of fluorine. As indicated below, this result is in accordance with the nuclear structure, isotopic constitution, and stability attributed to these elements.

Of the three hydrogen isotopes, the lightest one is predominantly abundant in normal hydrogen, the heaviest isotope, T_1^3 , being present in only infinitesimal amount. As a result, when hydrogen is bombarded with neutrons, though very occasionally interaction with a D_1^2 or a T_1^3 nucleus is possible, for the most part the bombarding neutrons will interact with protons, and as the majority of collisions between neutrons and hydrogen nuclei are elastic, no new nuclei are produced, *i.e.*, there is no induced radioactivity. In a small number of such collisions a neutron may be captured to form D_1^2 (though the probability of such an action is small), and in consequence γ -radiation may be emitted corresponding to the mass defect of D_1^2 with respect to H_1^1 and a neutron. Since this reaction results in the formation of a stable nucleus, no β -radioactivity should be observed as a result of interactions between neutrons and protons.

Similarly, interaction between a diplon and a bombarding neutron could result in the production of T_1^3 by capture of a neutron of low energy, though such an action would be difficult to observe experimentally, both on account of the small abundance of diplogen in normal hydrogen and also the unlikelihood of such a capture process under the normal experimental conditions. Many collisions between diplons and neutrons would be elastic and result in the production of recoil diplons, though on account of the small binding energy of the D_1^2 nucleus it is also likely that some nuclei will, on interaction with a high-energy neutron, disintegrate into their components. Thus no radioactivity could be observed as a result of interactions between neutrons and diplogen.

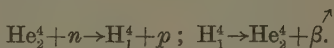
In a similar manner, neglecting elastic collisions, the disruption of T_1^3 by high-energy neutrons into D_1^2 and a neutron or into H_1^1 and two neutrons is possible. H_1^1 might be formed by neutron capture, but this is improbable. The nucleus H_1^1 is certainly β -radioactive, being spontaneously transformed to He_2^4 , thus :



and, on account of the great stability of He_2^4 , the isotope

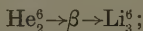
H_1^4 is probably of very short life, emitting high-energy disintegrating electrons. This, then, appears to be the only possible action whereby a β -radioactive isotope could be produced by bombarding hydrogen with neutrons, and it is, therefore, obvious why no induced radioactivity has been observed with this action.

The high mass defect of He_2^4 and all previous experimental work indicates that the α -particle is a particularly stable nucleus. In addition, the isotope He_2^5 , if stable, is present in terrestrial helium in minute quantity. In consequence all experimental work involving the neutron bombardment of helium can be considered as resulting in interactions between the bombarding particles and He_2^4 only. Hence, neglecting elastic collisions, which result in the production of recoil α -particles, two actions may occur, viz.: (a) the capture of a low-energy neutron and the production of He_2^5 , excess energy being emitted in the form of γ -radiation: this process would not give rise to any induced radioactivity; (b) neutron capture followed by proton emission, viz.,



But the α -particle is such a stable nucleus that this action is improbable, especially since it has recently been shown* that there exists a state of excitation of the α -particle of energy 12×10^6 e.v. Hence the great stability of He_2^4 accounts for the failure to detect β -radioactivity when helium is bombarded with neutrons.

He_2^6 may be formed when He_2^5 captures a neutron, the new nucleus being radioactive, thus:

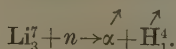
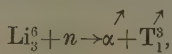


but not only is there little probability of such a capture process under the experimental conditions, but the very small abundance of He_2^5 would effectively prevent its detection.

The next element in the periodic table, lithium, consists of two isotopes of mass numbers 6 and 7, and, as shown previously, these nuclei may consist of an α -particle plus a diplon (Li_3^6), and an α -particle plus a diplon and

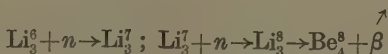
* Lauritsen and Crane, Phys. Rev. xlv. p. 537 (1934).

a neutron (virtually a T_1^3 nucleus), Li_3^7 *. Thus a high-energy neutron on interaction with lithium may eject the α -particle, the following reactions occurring :—



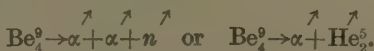
This is most likely, as Fermi † has shown that in general neutrons on interaction with the elements of odd atomic number cause the ejection of an α -particle, *e.g.*, N_7^{14} , F_9^{19} , Al_{13}^{27} , P_{15}^{31} , Cl_{17}^{35} , and Co_{27}^{59} .

Capture processes, though probably occurring with low-energy neutrons, are improbable with the neutrons from a Po-Be source among the elements of low atomic number, since, on account of the low potential barriers, any excess energy is usually emitted in the form of kinetic energy of a charged nuclear component. Hence, although the reactions



are probably important in the cosmic synthesis of the elements, in Fermi's experiments the bombarding energy of the neutrons was probably too great for such reactions to occur. Thus the only radioactive isotope produced is H_1^4 , and, as already suggested, this is probably of very short life. It is significant that Fermi obtained some slight evidence of radioactivity when lithium was bombarded with neutrons.

The recent experiments of Gentner ‡ on the ejection of neutrons from beryllium by γ -radiation indicate that Be_4^9 has a mass defect energy, of 0.45×10^6 e.v. In view of this low binding energy beryllium is a stable, although only just stable, nuclear unit, and it is, therefore, probable that high-energy neutrons will disrupt this nucleus into its components, and so Be_4^9 will be disintegrated by a non-capture process of the form

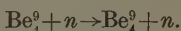


* Walke, *Phil. Mag.* xvii. p. 795 (1934).

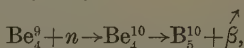
† Fermi, *Proc. Roy. Soc. A*, cxlvi. p. 483 (1934).

‡ Gentner, *Comptes Rendus* cxcix. p. 1211 (1934).

The ease with which beryllium can be made to yield neutrons suggests that neutrons might be emitted corresponding to the capture of the incident neutron and the emission of the nuclear neutron by the action

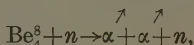


Alternatively, neutron capture with the formation of Be_4^{10} may take place, viz.,

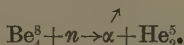


but this action is unlikely for the reasons already discussed, and under the experimental conditions used by Fermi this action does not take place.

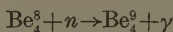
Similarly, since Be_4^8 is probably only just stable (if it exists at all), interactions between neutrons and this nucleus would lead to the non-capture disintegration



or to the capture disintegration

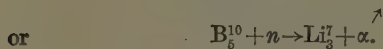
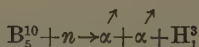


Also the action



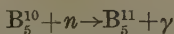
is possible. In any case it is obvious from these reactions that, even if Be_4^8 were an abundant isotope, no radioactive effect would be observed when this isotope is bombarded with neutrons. Since, however, its terrestrial existence is still unconfirmed, we conclude that the failure to observe β -radioactivity when beryllium is bombarded with neutrons is due to the small value of the binding energy of the constituent particles and consequently its easy disintegration into α -particles and a neutron.

The case of boron is similar to that of lithium. Assuming the nuclear structure* $\text{B}_5^{10} = \{[2\alpha] + (p + \bar{n})\}$ and $\text{B}_5^{11} = \{[2\alpha] + (p + \bar{n} + n)\}$, it appears likely that high-energy neutrons will disrupt the 2α -particle core as follows:—



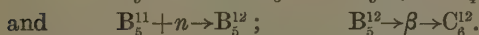
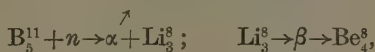
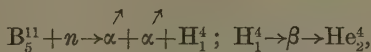
* Walke, *loc. cit.*

The capture process



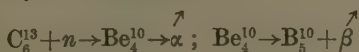
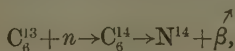
may also occur, though it is unlikely to be observed experimentally. Adopting the structural scheme suggested, we should, therefore, not expect induced β -radioactivity when B_5^{10} is bombarded with neutrons.

On the other hand, the corresponding disintegration of B_5^{11} would be

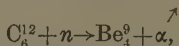


The capture process does not occur under the experimental conditions, since the bombarding neutrons have about $2-4 \times 10^6$ e.v. energy, and we can, therefore, neglect any radioactivity due to B_5^{12} . The other two reactions are, however, both probable, and β -radioactivity should be observed with boron. Fermi has observed slight indications of β -radioactivity of boron under neutron bombardment. If H_1^4 is short-lived, as suggested, the electrons due to the first reaction might not easily be observed, especially if the life of H_1^4 is of the order one second or less. In addition, the β -radioactivity of Li_3^8 would probably be very weak, as the mass defect energy of Be_4^8 is so small that the difference between the binding energies of Li_3^8 and Be_4^8 (which is equal to the maximum energy of the β -rays emitted) would be very small. All these facts operate against the detection of any β -radioactivity.

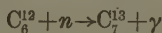
The failure to detect β -radioactivity in carbon is connected with its isotopic constitution and nuclear stability. The rarer isotope C_6^{13} exists in such small relative abundance that neutron reactions involving this isotope are probably so rare that they can be neglected as not being detectable under the experimental conditions used by Fermi. The reactions



are possible, but the abundance of C_6^{13} is such as to render difficult the detection of the resulting radioactivity. Moreover, the great stability of C_6^{12} , as indicated by the behaviour of carbon under bombardment by various nuclear projectiles and by its mass defect, indicates that C_6^{12} consists of a stable nuclear configuration of three α -particles. Thus, under neutron bombardment the predominant reaction* is as follows:—

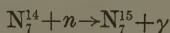


an α -particle being emitted after capture of the bombarding neutron. The capture process

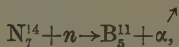


is permissible, but probably only occurs to a very small extent. It is thus apparent that no induced β -radioactivity would be observed by bombarding carbon with neutrons under experimental conditions as employed by Fermi.

The case of nitrogen is interesting, since there is indirect evidence that induced β -radioactivity will probably be observed if nitrogen in a suitable form, *i.e.*, NH_4NO_3 , is bombarded with neutrons. Like carbon, nitrogen consists of two isotopes, one of which, N_7^{15} , is present in such very small abundance that we can neglect nuclear reactions involving N_7^{15} , so that, in considering the disintegration of nitrogen under neutron bombardment, attention need only be directed to the isotope N_7^{14} . Of the possible reactions the capture process



cannot result in any radioactivity. Similarly, the more usual form of disintegration†,

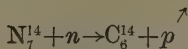
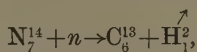


gives no induced β -radioactivity, since B_5^{11} is a stable nucleus.

* Harkins, Gans, and Newson, *Phys. Rev.* xliv. p. 236 (1933).

† Feather, *Proc. Roy. Soc. A*, cxxxvi. p. 709 (1932).

With nitrogen, however, the results of Kurie * and Feather † suggest that either of the reactions



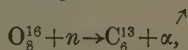
may occur, and although Feather, in discussing his results, indicates that the first is more likely, the second is definitely a possible reaction. The nucleus C_6^{14} is β -radioactive, and β weak radioactivity due to C_6^{14} may be detected if a suitable ammonium salt were bombarded with neutrons.

The case of oxygen resembles that of carbon, since the experiments on nuclear transmutation suggest that oxygen O_8^{16} is a particularly stable nucleus, probably consisting of a close combination of four α -particles. In addition, since O_8^{17} and O_8^{18} exist in very small abundance, nuclear reactions involving these isotopes are likely to occur infrequently, and although the capture process

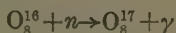


is necessary to explain the absence of O_8^{19} and the synthesis of fluorine from oxygen, it is improbable that induced β -radioactivity would be observed under the given experimental conditions because of the less abundant isotopes.

Photographs of the disintegration of oxygen by neutrons suggest that the predominant reaction involves the emission of α -particles, *e. g.*,



and such a reaction produces a stable C_6^{13} nucleus. Moreover, the possible process



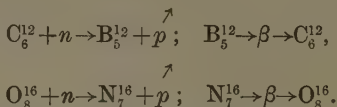
gives rise to a stable isotope. Thus induced β -radioactivity is unlikely to be observed with oxygen.

The ejection of a proton from either of the nuclei C_6^{12}

* Kurie, Phys. Rev. xlv. p. 904 (1934).

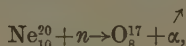
† Feather, *loc. cit.*

or O_8^{16} would give rise to a short-lived β -radioactive isotope, as follows :—



However, if (as seems probable) these nuclei consist of stable α -particle configurations, these reactions are precluded.

Experimental evidence is also against the production of induced radioactivity by bombarding neon with neutrons, as Harkins, Gans, and Newson have shown that the most usual disintegration of neon is by the reaction



and this results in the formation of a stable nucleus.

Hence the failure to observe β -radioactivity when the light elements are bombarded with neutrons is explained by their nuclear structure and isotope configurations.

XIX. *The Electric Moments of the Alkyl Monohalides.*

By P. C. MAHANTI, M.Sc., Lecturer, Applied Physics Department, University of Calcutta*.

ABSTRACT.

THE temperature sensitivity of the dielectric constants of the vapours of the methyl, ethyl, and propyl halides and of allyl chloride has been measured by means of a sensitive heterodyne beat apparatus, with a view to obtain accurate values for their electric moments. The results obtained are in accordance with the previously advanced hypothesis of an inductive effect.

Introduction.

ON an examination of the electric moments of monohydric alcohols⁽¹⁾ from the viewpoint of the theory of induced moments proposed by J. J. Thomson⁽²⁾ one is led to infer the absence of such moments in molecules

* Communicated by Prof. P. N. Ghosh, M.A., Ph.D., Sc.D.

since these alcohols have a moment whose value is unaffected by the position of OH radical, the length of the carbon chain, or its branching in them. But there is a possibility that the doublet associated with OH radical is not strong enough to appreciably affect the molecule; and one may reasonably expect that the introduction of a heavier component, *e. g.*, a halogen atom in place of OH radical, would enable one to study the effect of secondary moment. With this object in view the determination of electric moments of homologous alkyl monohalides by measuring the dielectric constants of their vapours was taken up in 1928. The results of these measurements, which were then published in two series of papers, were somewhat anomalous.

In the earlier paper ⁽³⁾ only the moments of ethyl bromide, methyl, and ethyl iodides were reported. A definite increase in moment from the methyl to the ethyl iodide was noticed. The values found for ethyl bromide and iodide were in fair agreement with those determined by Smyth ⁽⁴⁾ and his co-workers in the liquid state by means of a capacity bridge method. The measurements of Sircar ⁽⁵⁾ on methyl and ethyl chlorides also showed an increase in moment with the lengthening of the carbon chain, although his value for methyl chloride was considerably lower than that previously reported by Sanger ⁽⁶⁾. Almost simultaneously Williams ⁽⁷⁾ published his measurements on methyl and ethyl iodides in solution, and Hojendahl ⁽⁸⁾, his evaluation of the moments of a number of alkyl monohalides from the dielectric constants of their vapours at a single temperature using the old data of Pohrt ⁽⁹⁾. The results of these investigators also showed that the moments of the ethyl halides are decidedly higher than those of the corresponding methyl halides, while the moments of the members of the higher homologues were not sensibly different from them.

In the later paper ⁽¹⁰⁾ the moments of the methyl, ethyl, and propyl chlorides, bromides, and iodides and of allyl chloride were published. These results were not in conformity with the earlier determinations, in as far as they showed that the moments of the methyl halides were not sensibly different from those of the corresponding ethyl or propyl halides. The only questionable point was the assumption of the ordinary gas laws

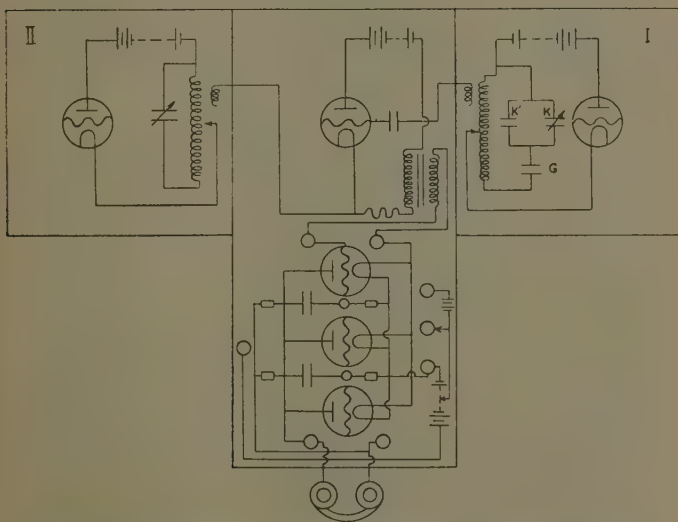
introduced into Debye's equation for the molecular polarization in order to eliminate the density factor at the various temperatures. This will lead to slightly lower values for the moments in all cases, but that does not explain the apparent discrepancy. On the other hand, it was found that moments reported for ethyl and propyl chlorides were in good agreement with the more accurately determined values of Sanger ⁽¹¹⁾ and Fuchs ⁽¹²⁾, while in the case of methyl chloride their values were decidedly lower than that given in the aforesaid paper. One is therefore led to doubt the purity of the chemicals used in the investigation. It is quite probable that the plates of the experimental condenser have been acted upon by these vapours, thereby introducing an anomaly in the measurements. In the same year Morgan and Lowry ⁽¹³⁾ determined the moments of the methyl halides in solution; and their value for methyl chloride was in close agreement with that of Sircar, while for the iodide it agreed well with the value of the moment reported by the author in the earlier paper. In view of these discrepancies it was desirable to undertake fresh measurements of the moments of the methyl, ethyl, and propyl halides in their vapour state. For this purpose Kahlbaum's and Merck's chemically pure materials were used. These were carefully dried over calcium chloride and phosphorus pentoxide, and finally fractionally distilled, the first and last portions of the distillate being rejected. The nickel plates of the experimental condenser used in the earlier determinations were gold-plated.

Experimental.

A heterodyne method, first suggested by Preuner and Pungs ⁽¹⁴⁾, was used to determine the dielectric constants of the vapours. The arrangement consists of three oscillating circuits. Two of these are high-frequency valve generators which are loosely coupled with one another; the third is also a valve generator, but is used to maintain a tuning-fork of 1024 frequency. A diagram of measuring circuits is shown in fig. 1. The two circuits I and II are coupled electromagnetically to a detector amplifier circuit, comprising an amplifier electron tube and a Telefunken Arcolette set. The

oscillator tubes are Telefunken R.E. 144 valves operating at 100 volts on the plate and about 4 volts on the filament. The amplifier tube is Telefunken R.E. .073 *d* valve operating at 15 volts on the plate and about 3 volts on the filament. Owing to the special characteristics of the valves used no grid bias is necessary, thus avoiding one possible source of error. The characteristic of each valve is very straight under the operating conditions. The tube used in the generator circuit for maintaining the tuning-

Fig. 1.



fork is Phillips B 403 valve, which is found to operate very satisfactorily during the period of this investigation.

The various parts of the measuring circuits are properly shielded from stray capacity effect by enclosing the apparatus in metal boxes made of zinc sheet and properly earthed. The two generator circuits and the detector amplifier circuit are separately enclosed. All the connexions are made by means of solid copper rods. Glazite wires were also used in certain cases. Special care was taken to keep all the coils, insulations, and resistances dry by enclosing calcium chloride vessels inside the boxes. All the variable condensers are operated from

outside by means of insulated shafts running through the shielding boxes. In order to compensate for possible changes in the circuits with time, the distributed capacity of the generator circuit II is varied from outside by means of a rod with a small brass disk attached to it inside the shielding box fitted through an ebonite tube. Small changes in frequency can be obtained by turning this brass rod, and thus varying the distance of the small disk from the generator circuit.

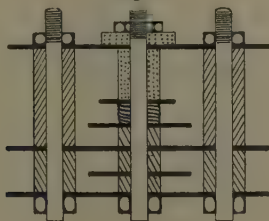
The frequency of the generator circuit I is of the order of 15×10^6 per second. The final selection of this order of frequency is made by trying several other frequencies. It is well known that the sensitiveness of the arrangement will be increased with increase in the frequency of the oscillating circuits; but at higher frequencies the oscillations are susceptible to the slightest change in their own circuits. Hence the choice of the particular frequency is made when the circuits are not liable to such slight changes but at the same time are sensitive enough to detect the small change desired for in the investigation. When using the apparatus the frequency of the generator I is kept constant, while the generator II is adjusted to have a frequency differing by about 1000 from that of generator I. The choice of this particular frequency difference has also been made after a series of trials. A tuning-fork of 1024 frequency is chosen for the purpose of comparison with the beat-tone of the oscillating circuits and to secure the no-beat condition at the time of observation.

The system of condensers used in the generator circuit I consists of three condensers, K, K', and C, as shown in fig. 1. K' is a Dubilier mica condenser, type 620, and K is a variable air condenser of the Bureau of Standards pattern, manufactured by Leeds and Northrup and standardized at the Bureau of Standards. C is the experimental condenser. As brass, copper, and even pure nickel were found to be acted upon by the organic vapours under investigation gold-plated nickel is chosen for the material of the condenser plates. For the sake of lightness and ease in manipulation the type of parallel plate system with quartz insulator is finally adopted. Fig. 2 shows the disposition of the condenser system. This was sealed in a pyrex-glass tube fitted with a stop-cock, and is connected to the pump and gas system. The

two platinum leads are sealed at the top of the glass tube and then connected to the generator circuit I.

The liquids whose boiling-points were above the room-temperature were introduced in a small bulb fitted with a stopcock after completely evacuating the air within it. It was then connected with the glass tube containing the experimental condenser and mercury manometer. The whole system was then evacuated with the pump, the stopcock of the bulb being kept closed. The stopcock was then opened for a very short time, the vapour passed into the condenser and the connecting systems. It was again pumped out, and vapour again introduced. The process was carried out six to seven times, so as to ensure that the system contains only the

Fig. 2.



vapour. For liquids whose boiling-points were lower than the room-temperature a different arrangement was made. A stout-glass vessel, the mouth of which was closed with a rubber cork fitted with a stopcock and perfectly sealed, contained the small phial of the compound under investigation. It was perfectly evacuated, and finally disconnected from the pump-system with the stopcock closed. The phial was then broken by giving the vessel a slight shock. The latter was subsequently connected with the manometer and the tube containing the experimental condenser.

The accurate determination of the dielectric constants depends as much on a careful calibration of the condensers used in the generator circuit I as on a steady and an accurate measurement of temperature, as well as on the correct estimation of pressure of the vapour at the time of observation. The calibration of the fixed and experimental condensers was made in terms of the standard

condenser by the method of substitution. The gross values (C) of the condenser determined by this method were found to be $122.4 \mu\mu$ F. The capacity of its leads was determined by constructing two dummy leads of the same length, and disposing them in the same manner as the actual leads, and found to be $4.2 \mu\mu$ F. This lead capacity is not altered by the influx of gas into the experimental condenser. Hence the effective value of the experimental condenser is $C_0 = 118.2 \mu\mu$ F. To avoid the effect of stray capacity, due to the presence of conductors near the experimental condenser, the method of measuring temperature by wrapping a platinum wire round it was not adopted. A copper-constantan thermocouple in conjunction with a voltage sensitive galvanometer, a potentiometer, and a Weston standard cadmium cell was used. The potential drop per cm. of the potentiometer wire was so adjusted that a change of temperature of 0.1° C. could easily be detected. It is, however, to be noted that the steadiness of temperature is of more importance than its absolute value. For this purpose an oil-bath of large capacity, heated electrically, was used. The temperature control of the bath was found to be very satisfactory. In order to be sure of the steadiness of temperature the bath was allowed to be heated at a particular current for at least twenty hours before an observation could be taken, and stirred electrically by means of a small motor. It is only when the temperature was found to be steady that an observation was started. Thus the measurement of dielectric constant at a single temperature could only be done per day. The pressure of the gas in the experimental condenser at the time of observation is read to an accuracy of about 0.5 mm. from the height of mercury manometer attached to the system by means of a kathetometer. The steadiness of temperature of the bath being ascertained, the oscillations are started, and allowed to run for at least half-an-hour previous to taking any observation, in order to be sure that the circuit conditions are steady. When this condition is attained the condenser is evacuated to 0.001 mm. The bath is then switched off the mains, the thermocouple is taken out of it, and the beat frequency of the two generating circuits is adjusted, as already stated, to get the no-beat condition between the frequency of tuning-fork and that of the generator circuit I with

the standard condenser at a definite setting. The vapour is next introduced into the experimental condenser, and the setting of the standard condenser adjusted till no-beat condition is restored in the telephone. The pressure of the vapour inside the experimental condenser is determined by noting the mercury levels in the manometer tube before and after the introduction of the vapour. The condenser is again evacuated and the bath switched on to the mains to get it ready for the next observation. Each observation is completed nearly within three minutes under perfectly steady conditions of the circuits. At each temperature generally five to ten observations were made under different pressures of the vapour inside the experimental condenser. The readings were usually taken during the calm hours of the night, when there is no external source of disturbance in the building. The slightest change from the condition of zero-beats in the telephone could easily be detected.

Finally, the value of $\epsilon-1$ at each temperature and pressure of the vapour has been calculated after the method of Zahn ⁽¹⁵⁾, and is given by

$$\epsilon-1 = 126.7 \frac{\Delta K}{\{K + \frac{1}{2}\Delta K + K'\}^2}.$$

Experimental Results.

The correctness of calibration of the apparatus was checked by determining the dielectric constant of dry and carbon-dioxide free air at 26.2° C. each time a new vapour was studied. When reduced to N.T.P. the mean of these several observations gave a value for $\epsilon=1.005722$, the mutual difference among them being very small. Table I. includes the results of the new measurements.

TABLE I.

Compound.	T°.	$\frac{(\epsilon-1)PT}{PT_0}$.	γ .
Methyl chloride.....	307.0	0.01092	3.35
	328.0	0.01034	3.39
	362.0	0.00954	3.45
	388.0	0.00902	3.50
	414.0	0.00857	3.55

TABLE I. (*cont.*).

Compound.	T°.	$\frac{(\epsilon-1)PT}{PT_0}$.	y .
Methyl bromide	303.0	0.01046	3.17
	325.0	0.00989	3.21
	356.0	0.00921	3.28
	389.0	0.00861	3.35
	417.0	0.00817	3.41
Methyl iodide	304.0	0.00957	2.94
	326.0	0.00920	3.00
	356.0	0.00865	3.08
	394.0	0.00810	3.19
	416.0	0.00781	3.25
Ethyl chloride	304.0	0.01355	4.12
	335.0	0.01254	4.20
	367.2	0.01169	4.29
	395.9	0.01104	4.37
	420.5	0.01054	4.43
Ethyl bromide	301.0	0.01375	4.14
	333.0	0.01270	4.23
	357.0	0.01204	4.30
	392.0	0.01122	4.40
	420.0	0.01066	4.48
Ethyl iodide	306.0	0.01349	4.13
	326.0	0.01291	4.20
	350.0	0.01223	4.28
	374.0	0.01165	4.36
	404.0	0.01104	4.46
<i>n</i> -Propyl chloride	304.0	0.01428	4.34
	310.0	0.01406	4.36
	337.4	0.01316	4.44
	378.2	0.01206	4.56
	402.0	0.01152	4.63
<i>n</i> -Propyl bromide	302.0	0.01427	4.31
	327.0	0.01342	4.39
	352.0	0.01270	4.47
	384.0	0.01190	4.57
	416.0	0.01123	4.67
<i>n</i> -Propyl iodide	305.0	0.01419	4.33
	323.0	0.01359	4.39
	351.0	0.01281	4.50
	379.0	0.01213	4.60
	404.0	0.01161	4.69
Allyl chloride	304.0	0.01405	4.27
	343.4	0.01278	4.39
	384.0	0.01174	4.51
	393.0	0.01155	4.54
	420.0	0.01100	4.62

Calculation of Electric Moments.

According to Debye⁽¹⁶⁾ the molar polarization, P , of a molecule having an electric moment, μ , is given by

$$P = \frac{4\pi}{3} N \left(\alpha_0 + \frac{\mu^2}{3KT} \right), \quad \dots \quad (1)$$

where N is the Avogadro number ($= 6.06 \times 10^{23}$), K the Boltzmann constant ($= 1.37 \times 10^{-16}$), and T the absolute temperature. The factor α_0 represents the distortion effect, while the factor $\frac{\mu^2}{3KT}$ stands for the orientation effect.

Assuming that the assumptions about the internal field made by Clausius and Mosotti are justified in the case of vapours of small density, the molar polarization, P , can also be expressed in the form

$$P = \frac{\epsilon - 1}{3} \cdot \frac{M}{\rho}, \quad \dots \quad (2)$$

where ϵ is the dielectric constant, M the molecular weight, and ρ the density of the vapour corresponding to the temperature T .

Now combining the equations (1) and (2) we get

$$\frac{\epsilon - 1}{3} \cdot \frac{M}{\rho} = \frac{4\pi}{3} N \left(\alpha_0 + \frac{\mu^2}{3KT} \right). \quad \dots \quad (3)$$

If we assume, further, that the vapours obey ordinary gas laws, then

$$\frac{1}{\rho} = \frac{1}{\rho_0} \cdot \frac{P_0 T}{P T_0},$$

so that
$$\frac{(\epsilon - 1) P_0 T}{P T_0} = \frac{4\pi N P_0}{M} \cdot \left(\alpha_0 + \frac{\mu^2}{3KT} \right).$$

Putting
$$A = \frac{4\pi N \rho_0}{M} \cdot \alpha_0, \quad \dots \quad (4 a)$$

$$B = \frac{4\pi N \rho_0}{M} \cdot \frac{\mu^2}{3KT}, \quad \dots \quad (4 b)$$

and
$$y' = \frac{(\epsilon - 1) P_0 T}{P T_0}, \quad \dots \quad (4 c)$$

we have
$$y' = A + \frac{B}{T},$$

$$\begin{aligned}
 i. e., \quad & y'T = AT + B, \\
 \text{or} \quad & y = AT + B, \quad . \quad . \quad . \quad . \quad . \quad (5) \\
 \text{where} \quad & y = y'T.
 \end{aligned}$$

It is evident from equation (5) that when the values of y are plotted against those of T we shall get a straight line whose slope will give us the measure of A and whose intercept on the y -axis the value of B .

Knowing B we can calculate the electric moment, μ , of the molecule from equation (4 b), and is given by

$$\mu^2 = 1.208 \times 10^{-36} B. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The values of A , B and μ for the different alkyl halides studied in this paper are given in Table II.

TABLE II.

Compound.	A.	B.	$\mu \times 10^{18}$.
CH ₃ Cl	0.001852	2.77	1.83
C ₂ H ₅ Cl	0.002667	3.31	2.00
C ₃ H ₇ Cl	0.002966	3.37	2.02
<i>n</i> -C ₃ H ₇ Cl	0.002900	3.46	2.04
CH ₃ Br	0.002075	2.54	1.75
C ₂ H ₅ Br	0.002857	3.28	1.99
<i>n</i> -C ₃ H ₇ Br	0.003151	3.36	2.01
CH ₃ I	0.002730	2.11	1.60
C ₂ H ₅ I	0.003380	3.10	1.93
<i>n</i> -C ₃ H ₇ I	0.003652	3.21	1.97

It may here be noted that, as in earlier measurements, the error in the polarization values, owing to the use of the ideal gas law in their calculation, has not been eliminated; consequently the values of electric moments are expected to be very slightly lower than those calculated after eliminating this source of error.

The error is, however, minimized when the measurements are done at high temperatures and low densities of the vapours; in fact, the values of electric moments given in Table II. do not differ in any case by more than 1.7 per cent. from those more accurately determined by Sanger, Fuchs, and by Smyth and McAlpine ⁽¹⁷⁾ for some of these molecules. The new measurements reveal

further that only in the case of methyl chloride, ethyl, and propyl bromides and iodides the earlier determinations were uncertain.

Interpretation of Results.

The values of electric moments for the methyl, ethyl, and *n*-propyl halides given in Table II. indicate definitely that the induction effect due to the principal doublet associated with the carbon-halogen bond of a normal primary alkyl halide molecule is transmitted as far as the second carbon atom of the chain. Beyond the second carbon the effect is not of any appreciable magnitude. As a consequence the electric moments of the ethyl halides are higher than those of the corresponding methyl compounds, while the *n*-propyl halides have moments not appreciably different from the former. Hence in the case of the remaining higher homologues of the series identical values of moments may be expected. It is to be noted further that even when the carbon bond is unsaturated, as in allyl chloride, the induction effect does not undergo any appreciable change. Meanwhile Werner⁽¹⁸⁾ has measured the electric moments of the aliphatic cyanides in solution, and has observed increase in moment due to the induction effect as far as the third member of the series. He has further pointed out that their moments may be represented by an exponential series which converges at about C_5 or C_6 with the limiting value of $\mu = 3.56 \times 10^{-18}$.

From the increase in moment from the methyl to the ethyl halides one may also expect that in secondary or tertiary halides, where the branching of the chain occurs at the carbon atom adjacent to the halide atom, the moments should have values higher than those of their primary compounds. In the case of the secondary compounds besides the carbon atom in the α -position which forms a part of the main doublet two other carbon atoms in the β -positions are equally affected by induction, thereby increasing the moments of the molecules as a whole, so that their magnitudes should be greater than those of the corresponding primary compounds. In tertiary halides since there is one more carbon atom in the β -position than in their secondary compounds it is natural to expect that their moments should even

be higher than those of the latter. On the other hand, if the branching of the chain occurs at a carbon other than the α -carbon atom, no increase in moment will be noticed. Consequently the electric moments of this class of secondary and tertiary halides will be indistinguishable from those of the corresponding primary compounds. It is now of interest to enquire how the moments of the alkyl halides will be influenced by changing the position of the halogen in them. It is evident that in primary halides other than methyl and ethyl the linking of the halogen to the end carbon atoms (*i. e.*, to the α -carbon in the chain) in any position will not alter their moments from those of their corresponding normal compounds—in other words, they will not be appreciably different from the moments of ethyl halides. On the other hand, when the halogen is linked to any carbon atom other than the end carbon in a primary halide the moment will be identical with that of its secondary compound. Likewise one would expect that if the position of the carbon is changed in a secondary alkyl halide the moment will either be equal to that of the corresponding normal secondary or tertiary compound. Data⁽¹⁹⁾ of the electric moments are now available for some of the iso- as well as secondary and tertiary alkyl halides of the higher homologues in their liquid state. For the iso-propyl halides it is evident from the results of Parts that the values of their moments are definitely higher than those of their normal primary compounds, since in the case of these iso-compounds two β -carbon atoms are affected by induction, in addition to the α -carbon forming a part of the main doublet. In the case of the butyl- and amyl-halides it is also apparent from the results of the same investigator that, while the iso-halides have moments equal in magnitude to those of their normal primary compounds, those of secondary halides are higher, while their tertiary compounds have still higher values of electric moments. For primary heptyl halides Errera and Sherrill have found that when the halogen is linked to a carbon other than the end carbon in the chain the value of the moment is increased but remains constant for the different positions of the halogen in them.

The results of this present investigation, in conjunction with those of other investigators, prove definitely the validity of the hypothesis of an induction effect. One is

led to conclude that the electric moment of a homologous series increases with the length of the carbon chain or remains constant, according as the main doublet, developed by the introduction of an atom or radical into the hydrocarbons, is sufficiently strong to induce secondary doublets of any appreciable magnitude in the rest of the molecule or not. Hence the hypothesis of the constancy of the group moment, which is characteristic of the substituent in question, is only in qualitative agreement with the experimental results, and fails to account for the latter quantitatively. In fact, both the magnitude and direction of the group moment are dependent on the nature of the rest of the molecule.

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References.

- (1) P. C. Mahanti and R. N. Das Gupta, *Ind. Journ. Phys.* iii. p. 467 (1929); C. P. Smyth and W. N. Stoops, *J. Am. Chem. Soc.* li. p. 3330 (1929); J. Errera and M. L. Sherrill, *J. Am. Chem. Soc.* lii. p. 1993 (1930); C. P. Smyth and R. W. Dornte, *J. Am. Chem. Soc.* liii. p. 545 (1931); P. C. Mahanti, *Zeits. f. Physik* (in the press).
- (2) J. J. Thomson, *Phil. Mag.* xlv. p. 497 (1923).
- (3) P. C. Mahanti and D. N. Das Gupta, *Ind. Journ. Phys.* iii. p. 181 (1928).
- (4) C. P. Smyth and S. O. Morgan, *J. Am. Chem. Soc.* l. p. 1547 (1928); C. P. Smyth and W. N. Stoops, *J. Am. Chem. Soc.* li. p. 3312 (1929).
- (5) S. C. Sircar, *Ind. Journ. Phys.* iii. p. 197 (1928).
- (6) R. Sanger, *Phys. Zeits.* xxvii. p. 536 (1926).
- (7) J. W. Williams, *Zeits. Physik. Chem.* cxxxviii. A, p. 75 (1928).
- (8) K. Hojendahl, Thesis, Copenhagen (1928).
- (9) G. Pohrt, *Ann. d. Physik*, xlii. p. 569 (1913).
- (10) P. C. Mahanti, *Phys. Zeits.* xxxi. p. 546 (1930).
- (11) R. Sanger, *Helv. Phys. Acta.* iii. p. 161 (1930).
- (12) O. Fuchs, *Zeits. f. Physik.* lxiii. p. 824 (1930).
- (13) S. O. Morgan and H. H. Lowry, *J. Phys. Chem.* xxxiv. p. 2385 (1930).
- (14) G. Preuner and L. Pungs, *Phys. Zeits.* xx. p. 543 (1919).
- (15) C. T. Zahn, *Phys. Rev.* xxiv. p. 400 (1924).
- (16) P. Debye, *Phys. Zeits.* xiii. p. 97 (1912).
- (17) C. P. Smyth and K. B. McAlpine, *J. Chem. Phys.* ii. p. 499 (1924).
- (18) O. Werner, *Zeits. Physik. Chem.* B, iv. p. 371 (1929).
- (19) A. Parts, *Zeits. Physik. Chem.* B, vii. p. 327 (1930); xii. p. 312 (1931); J. Errera and M. L. Sherrill, *J. Amer. Chem. Soc.* lii. p. 1993 (1930).

XX. *Characteristic Values of the Mathieu Equation.*
 By D. H. WEINSTEIN, Ph.D., California Institute of
 Technology*.

1. We take the Mathieu equation ⁽¹⁾ to be of the form

$$\frac{d^2u}{dx^2} + (a + 16q \cos 2x)u = 0, \quad . \quad . \quad . \quad (1)$$

where a and q are constants. According to the well-known theorem by Floquet, the general solution of the Mathieu equation is of the form

$$\mu = c_1 e^{\mu x} \phi(x) + c_2 e^{-\mu x} \phi(-x),$$

where $\phi(x)$ is a periodic function with period 2π , and c_1 and c_2 are arbitrary constants of integration, μ is a function of a and q only. The constant a is known as the characteristic value, and the constant μ is known as the characteristic exponent.

We wish to consider the problem of determining a as a function of μ , q . Analytically, explicit expressions for a have been given in the form of infinite series which, however, have the characteristic feature that the general m th term is not known. For this reason, a discussion of the convergence is difficult; in fact, no satisfactory discussion has yet been given. In the case, for example, of $\mu=0$, $n>3$, these series are as follows if we stop at q^2 :

$$a_n = n^2 + \frac{32q^2}{n^2-1} + \dots \quad . \quad . \quad . \quad (2)$$

We are going to give, therefore, some finite expressions for a as a function of μ , q , together with a remainder, when μ is purely imaginary (stable solutions). That is, instead of an infinite series, we give expressions analogous to Taylor's formula with a remainder. While it would be desirable, mathematically, to have similar expressions for the case that the real part of μ is not equal to zero, it suffices for physical problems to confine ourselves to the stable solutions only.

2. Let us take a particular solution of equation (1) in the form

$$u(x) = e^{i\nu x} \phi_{\nu n}(x), \quad . \quad . \quad . \quad (3)$$

* Communicated by the Author.

where ν is a wholly real constant, and $\phi_{\nu n}(x)$ is periodic in 2π . The subscript ν indicates the value of the characteristic exponent with which $\phi_{\nu n}$ is associated, and the subscript n indicates that $\phi_{\nu n}$ is the n th function ($n=0, 1, 2 \dots$) proper to ν .

The differential equation for $\phi_{\nu n}$ is

$$\frac{d^2\phi_{\nu n}}{dx^2} + 2i\nu \frac{d\phi_{\nu n}}{dx} + (a_{\nu n} - \nu^2 + 16q \cos 2x)\phi_{\nu n} = 0, \quad (4)$$

and for its conjugate complex

$$\frac{d^2\phi_{\nu n}^*}{dx^2} - 2i\nu \frac{d\phi_{\nu n}^*}{dx} + (a_{\nu n} - \nu^2 + 16q \cos 2x)\phi_{\nu n}^* = 0, \quad (5)$$

where $a_{\nu n}$ is the characteristic value associated with $\phi_{\nu n}$. We shall suppose that the $a_{\nu n}$ are arranged in order $a_{\nu 0} \leq a_{\nu 1} \leq a_{\nu 2} \dots$

When $\nu=0$, these functions reduce to Mathieu functions as follows :

$$\phi_{0, 2n} = ce_n; \quad \phi_{0, 2n+1} = se_{n+1}. \quad \dots \quad (6)$$

In the usual manner, it follows from equation (4) and equation (5) that we have the orthogonality conditions ⁽²⁾

$$\int_0^{2\pi} \phi_{\nu m}^*(x) \phi_{\nu n}(x) dx = 0 \quad (m \neq n). \quad \dots \quad (7)$$

Since it is not possible to obtain exact values for the $\phi_{\nu n}$, we are going to do what may be regarded in a sense as equivalent to obtaining exact values; namely, give approximate values together with outside limits for the errors. We can do this by means of a method recently described by us ⁽³⁾, and which goes to the following effect. If we have a characteristic value problem of the form

$$H\psi_n = W_n\psi_n, \quad \dots \quad (8)$$

where ψ_n is the n th characteristic function and W_n is the n th characteristic value, then if we take any arbitrary function ξ subject to the condition $\int \xi^* \xi d\tau = 1$ and the appropriate boundary conditions, we have

$$I_1 + \sqrt{I_1 - I_1^2} \geq W_j \geq I_1 - \sqrt{I_2 - I_1^2}, \quad \dots \quad (9)$$

where

$$I_1 = \int \xi^* H \xi d\tau; \quad I_2 = \int (H^* \xi^*)(H \xi) d\tau,$$

and W_j is that characteristic value to which I_1 is nearest (that is $(W_j - I_1)^2 \leq (W_n - I_1)^2$ for all n).

In the case that it is not known to which characteristic value W_j is nearest, equation (9) still asserts that the two limits enclose some one of the characteristic values, and this is quite sufficient for our purposes.

We observe that equation (4) is of the form

$$H\phi_{\nu\mu} = -a_{\nu\mu}\phi_{\nu\mu}, \quad . \quad . \quad . \quad . \quad (10)$$

where

$$H = \frac{d^2}{dx^2} + 2i\nu \frac{d}{dx} - \nu^2 + 16q \cos 2x.$$

Since this is of the same form as equation (8), and the $\phi_{\nu\mu}$ form a complete orthogonal set ⁽⁴⁾, we are in a position to apply the above theory.

3. We have from equation (9)

$$a_{\nu n} = -I_1 + \theta \sqrt{I_2 - I_1^2}, \quad . \quad . \quad . \quad . \quad (11)$$

where

$$\begin{aligned} I_1 &= \int_0^{2\pi} \xi_{\nu n}^* \left(\frac{d^2}{dx^2} + 2i\nu \frac{d}{dx} - \nu^2 + 16q \cos 2x \right) \xi_{\nu n} dx \\ I_2 &= \int_0^{2\pi} \left[\left(\frac{d^2}{dx^2} - 2i\nu \frac{d}{dx} - \nu^2 + 16q \cos 2x \right) \xi_{\nu u}^* \right] \\ &\quad \times \left[\left(\frac{d^2}{dx^2} + 2i\nu \frac{d}{dx} - \nu^2 + 16q \cos 2x \right) \xi_{\nu n} \right] dx, \end{aligned}$$

and θ ranges from $+1$ to -1 . We shall refer to the term $\sqrt{I_2 - I_1^2}$ as the error, although it is clearly the maximum possible error.

We must, however, remember to impose the proper conditions on the approximate function $\xi_{\nu n}$. In addition to being normalized, $\int \xi_{\nu n}^* \xi_{\nu n} dx = 1$, $\xi_{\nu n}$ must be periodic in 2π , because we want to get approximations to characteristic values proper to the fixed value of ν only. This necessarily follows from the Floquet theorem.

Since ξ must be periodic in 2π and quadratically integrable, we can take it to be of the form

$$\xi = \sum_{m=-\infty}^{\infty} b_m e^{imx}. \quad . \quad . \quad . \quad . \quad (12)$$

We are then to substitute in equation (12) and adjust the b_m so as to give us a suitably small error. One

general thing must be mentioned. The b_m need only be purely real. This follows from the following simple consideration. If a solution of equation (1) is $e^{i\nu x}\phi(x)$, then $e^{-i\nu x}\phi(-x)$ and $e^{-i\nu x}\phi^*(x)$ are also solutions. Putting $\phi(x)=\Sigma b_m e^{imx}$, we must have

$$\pm \Sigma b_m e^{-imx} = \Sigma b_m^* e^{-imx}. \quad . \quad . \quad . \quad (13)$$

Hence $b_m = \pm b_m^*$, or that is to say, aside from a constant factor, the b_m are all real.

The simplest possible case of the above is to take but one term. That is, let

$$\xi_{\nu n} = \frac{1}{\sqrt{2\pi}} e^{in x}. \quad . \quad . \quad . \quad (14)$$

Then one easily finds $I_1 = -(n+\nu)^2$, $\sqrt{I_2 - I_1^2} = 8\sqrt{2q}$.

Hence, we have

$$\alpha_{\nu n} = (n+\nu)^2 + \theta.8\sqrt{2q}. \quad . \quad . \quad . \quad (15)$$

In the case of $\nu=0$, we see that $-I_1$ gives us the first term of equation (2). This result for $\nu=0$ has been obtained by Ince ⁽⁵⁾, but with an error of $16q$ instead of $8\sqrt{2q}$. If we had used $\cos nx$ in place of the exponential above, then everything would be the same except for $n=1$, in which case $I_1 = (1+\nu)^2 \pm 8q$ and $\sqrt{I_2 - I_1^2} = 8q$. The upper sign refers to $\cos x$ and the lower $\sin x$. In this case the simplest uniform analytical expression for $\alpha_{\nu n}$ would be

$$\alpha_{\nu n} = (n+\nu)^2 + \theta.16q. \quad . \quad . \quad . \quad (16)$$

For $\nu=0$, we would thus have the identically same result as Ince.

We can also treat the generalized Mathieu equation with the same ease as the ordinary equation to this approximation. Thus, if in place of $16q \cos 2x$ we have an absolutely convergent Fourier series

$$\Sigma A_m \cos mx + B_m \sin mx,$$

then we find that

$$\alpha_{\nu n} = (n+\nu)^2 + \theta. \frac{h}{\sqrt{2}}, \quad . \quad . \quad . \quad (17)$$

where $h = \sqrt{\Sigma(A_m^2 + B_m^2)}$. Of course, this approximation is too crude for reasonable values of q . It may, how-

ever, be useful for some physical problems where one wishes to calculate quantities within a factor of 2, say.

4. We proceed now to consider the next approximation for the characteristic values of the ce_n and se_n .

Taking therefore

$$\xi_{0, 2n} = \left[1 + \frac{8q^2(n^2+1)}{(n^2-1)^2} \right]^{-\frac{1}{2}} \left[\cos nx - \frac{2q}{n-1} \cos(n-2)x + \frac{2q}{n+1} \cos(n+2)x \right]. \quad (18)$$

We find

$$\left. \begin{aligned} I_1 &= - \frac{n^2(n^2-1)^2 + 8q^2(n^4 + 5n^2 - 4)}{(n^2-1)^2 + 8q^2(n^2+1)} \\ \sqrt{I_2 - I_1^2} &= \frac{16\sqrt{2}q^2\sqrt{[(n^2-1)^2 + 8q^2(n^2+3)](n^2+1)}}{(n^2-1)^2 + 8q^2(n^2+1)} \end{aligned} \right\}. \quad (19)$$

If $-I_1$ is expanded in powers of q , then it will agree with equation (2) up to powers of q^2 . Equation (19) holds good for all n except $n=1$, and apply to both ce_n and se_n . It might appear that for $n < 4$, each case would have to be calculated separately. This is so, if somewhat more accurate expressions are wanted, but nevertheless, the above expressions are correct because one could substitute exponential functions in place of the cosines and obtain the same results without exceptions for $n < 4$.

We note that as n becomes large, $-I_1$ approaches n^2 and the error goes to zero as $\frac{16\sqrt{2}q^2}{n}$. Thus, the well-

known asymptotic feature of $\cos nx$ and $\sin nx$, and their manner of approach is clearly given. When $16q=1$, the error is $\cdot 026$, and when $16q=\frac{1}{2}$ it is $\cdot 006$.

So far we have not concerned ourselves with the convergence of the infinite series of section 1, since our results hold whether they converge or not. One might reasonably expect, however, that as q is increased, the value of q for which convergence fails would be indicated by the error of the higher approximations becoming larger than that of the lower approximations. A comparison of the first and second approximations, however, does not reveal any such behaviour except for $n=0$. For all other n the second approximation is smaller than the first, no matter how large q is. For $n=0$, the critical value of

q is .99, a value well past any possibility of convergence. We conclude, therefore, that any discussion of convergence will have to consider the error of an arbitrary number of approximations.

5. It is rather interesting to consider a case when q is very large and positive. Following the notation of Ince⁽⁶⁾, we set $32q=k^2$, and then we have equation (4) in the form, $\nu=0$,

$$\frac{d^2\phi}{dx^2} - k^2 \sin^2 x \phi = -A\phi, \quad . \quad . \quad . \quad (20)$$

where

$$A = a + \frac{1}{2}k^2.$$

Taking

$$\xi = \left[\int_0^{2\pi} e^{2k \cos x} dx \right]^{-\frac{1}{2}} e^{k \cos x}, \quad . \quad . \quad . \quad (21)$$

we find

$$\left. \begin{aligned} I_1 &= -k \left[\int_0^{2\pi} e^{2k \cos x} dx \right]^{-1} \int_0^{2\pi} e^{k \cos x} \cos x dx \\ I_2 &= k^2 \left[\int_0^{2\pi} e^{2k \cos x} dx \right]^{-1} \int_0^{2\pi} e^{2k \cos x} \cos^2 x dx \end{aligned} \right\}. \quad (22)$$

Making use of the integral

$$\int_0^{2\pi} e^{2k \cos x} dx = 2\pi J_0(-2ik), \quad . \quad . \quad . \quad (23)$$

we have

$$\left. \begin{aligned} I_1 &= -ik \frac{J_1(-2ik)}{J_0(-2ik)} \\ I_2 - I_1^2 &= k^2 \left[\frac{J_0^2(-2ik) + 2J_1^2(-2ik) - J_0(-2ik)J_2(-2ik)}{2J_0^2(-2ik)} \right] \end{aligned} \right\}. \quad (24)$$

Inasmuch as k is supposed to be large, we can use the asymptotic expansion for Bessel functions. Neglecting

$\frac{1}{k}$, we obtain

$$\left. \begin{aligned} I_1 &= -k + \frac{1}{4}; \quad \sqrt{I_2 - I_1^2} = \frac{1}{2\sqrt{2}} \\ a &= -\frac{1}{2}k^2 + k - \frac{1}{4} + \theta \cdot \frac{1}{2\sqrt{2}} \end{aligned} \right\}. \quad . \quad . \quad . \quad (25)$$

We note that the error becomes a constant as $k \rightarrow \infty$. That is to say, our approximate function does not become asymptotic as $k \rightarrow \infty$, but the residual error is small enough in some cases to be neglected. A comparison with Ince⁽⁶⁾ shows that we have obtained, so far as our development goes, his zeroth order characteristic value. Our approximate function is the main factor of his asymptotic solution, the whole of which is, however, not quadratically integrable, and therefore not suited for our method.

References.

- (1) M. J. O. Strutt, 'Ergebnisse Math. u. ihrer Grenzgebiete,' i. p. 199 (1932).
- (2) This is a special case of the more general orthogonality conditions

$$\int_0^{2\pi} \phi_{\mu m}(-x) \phi_{\mu n}(x) dx = 0 \quad (m \neq n).$$
- (3) D. H. Weinstein, Proc. Nat. Acad. xx. p. 529 (1934).
- (4) This argument is not essential, as recourse can be had to general variational arguments. See ref. 3 and also J. K. L. MacDonald, Phys. Rev. xvi. p. 828 (1934).
- (5) E. L. Ince, J. Lond. Math. Soc. ii. p. 46 (1927).
- (6) E. L. Ince, Proc. Roy. Soc. Edin. xvi. p. 316 (1926).

XXI. Attempts to detect γ -radiation excited by the Impact of α -particles on Heavy Elements. By W. B. LEWIS, Ph.D., and B. V. BOWDEN, Ph.D.*

IT is well known that the efficiency of production of γ -radiation by the impact of atomic projectiles on matter is exceedingly small, and a much smaller number of quanta is produced by a beam of protons than by electrons of the same energy. Cockcroft and Walton⁽¹⁾ have shown that for protons of 300 kv. energy the number of quanta is certainly less than one in 10^6 of those produced by the same number of electrons. Bothe and Becker⁽²⁾ made a systematic investigation of the radiations excited in several elements by the α -particles from polonium. They detected γ -radiation from several of the lighter elements, but in every instance the radiation could be associated with the disintegration by the α -particles of the nuclei of the target. These

* Communicated by Lord Rutherford, O.M., F.R.S.

results have been confirmed by Webster ⁽³⁾, who made similar experiments. The discovery of certain penetrating radiations produced in this way was the first experimental evidence for the existence of neutrons. Bothe and Becker detected no radiation which cannot now be explained as being associated with the atomic disintegration of some light element, and in particular they observed no trace of any radiation excited in the heavier elements. They conclude that the efficiency of production was considerably less than one quantum for 10^6 polonium α -particles incident on the lead. They remark that it is difficult to reconcile these results with certain experimental results of Slater ⁽⁴⁾, who observed γ -radiation of about 400,000 electron volts energy excited in lead by the impact of α -particles from radon, and who estimated that about one α -particle in 6000 was effective in producing a γ -ray. If these results are to be reconciled, the results of Slater must either be peculiar to the radiations from the disintegration of radon, or there must be a threshold α -particle velocity such that α -particles which have less than this critical velocity cannot excite hard γ -radiation in lead; and further, this threshold velocity, by a peculiar coincidence, must lie in the very small range between the velocities of radon and polonium α -particles, which differ in energy by only 170,000 electron volts in a total energy of about 5.5×10^6 electron volts.

It was to be expected that, if such a threshold velocity exists, a relatively great number of quanta would be excited by the much swifter α -particles from radium C'. Experiments, therefore, have been made to examine the effect of these particles. It will be realized that it is essential in such experiments to separate any secondary γ -radiation excited by the α -particles from the very intense primary γ -radiation emitted by the source. It was to avoid this difficulty that both Slater and Bothe and Becker used sources of α -particles which are accompanied by relatively small amounts of primary γ -radiation.

FIRST EXPERIMENT.—*The Annular Magnet.*

The annular magnet which we have used ⁽⁵⁾ for the measurements of the relative velocities of α -particle groups provided an intense beam of α -particles at a point which is separated from the source by a thickness of

iron and copper sufficient to absorb all the γ -radiation emitted by the active deposit of radium (B+C) used as the source in these experiments. A beam of 5×10^6 α -particles per minute was obtainable from a 50 mg. source of radium C'. If a single γ -ray quantum is produced in lead by 10,000 α -particles we should thus expect to have about 500 γ -ray quanta per minute, of which about 100 per minute might traverse a Geiger-Müller tube counter suitably mounted in the magnet gap.

The efficiency of a Geiger-Müller counter for γ -ray quanta may be estimated on the assumption that every β -ray which passes through the counter produces a discharge. In this optimum condition the efficiency is approximately equal to the ratio of the absorption coefficient of the primary γ -ray to that of the electrons which it liberates by Compton recoil ⁽⁶⁾. This ratio does not differ much from 0.6 per cent. for most metals over the range of γ -ray energies under consideration. The efficiency of the very short tube counters used in our experiments was found to be about half of this.

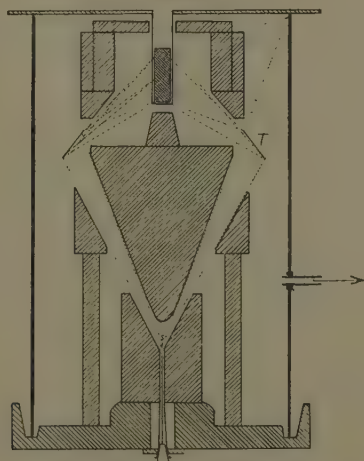
In an experiment made as already suggested, with a radium B+C source of 50 mg. equivalent, the number of discharges expected was thus about one in three minutes, on the assumption that one quantum is produced by 10,000 α -particles. The natural effect of the counter due to cosmic rays and other stray radiation was about three discharges in two minutes. There was no evidence of any effect as great as estimated by Slater, but any smaller effect might have escaped detection. It should be noted that as the α -particles were incident on a thick lead target this result applies to α -particles of all velocities up to the maximum from radium C', which includes the velocity of the radon α -particles. This result throws doubt on Slater's interpretation of his experiments, because it might reasonably be expected that the efficiency of production of γ -rays would increase rapidly with the velocity of the incident α -particles.

SECOND EXPERIMENT.—*Screening by Lead.*

In order to confirm this result, and to be able to detect even smaller amounts of radiation, a special apparatus was designed, using a larger target, so that it was possible to investigate the effect of α -particles emitted by the

source over a larger solid angle. This apparatus was arranged to have cylindrical symmetry and was in this respect somewhat similar to that used by Gray and Tarrant ⁽¹¹⁾ for the study of γ -radiation scattered through a certain angle from a primary beam. The target for the α -particles was, however, only a ring of metal foil. The screening of the counter was complicated, since it was necessary to place the apparatus in a container which could be evacuated, and the counter must then be screened from any γ -radiation scattered by the walls

Fig. 1.



of the container. The design illustrated in fig. 1 satisfies this requirement. The diagram represents a section through the apparatus, which is mounted on a heavy steel base, and is enclosed by a large bakelized paper cylinder surmounted by a steel disk. A brass well is lowered through a central hole in this disk and contains a large (10×3 cm.) Geiger-Müller tube counter. This mounting allows the counter to be changed readily and avoids all difficulty of introducing electrical leads at high potentials into the vacuum. The source *S* is introduced on the end of a rod through the base and passes up through a narrow hole in the lead cylinder shown. The upper portion of this cylinder is coned

out. The direct radiation from the source is screened from the counter and its surrounding lead shields by the large lead cone shown in the centre of the diagram. The design is such that, except in the annular conical space left for the α -particles, a thickness of at least 10 cm. of lead is interposed in all directions from the source to any scattering matter, and a thickness of 5 cm. of lead is interposed between the counter and any matter exposed to the unscreened γ -radiation from the source. A thickness of 37 cm. of lead screens the counter from the direct radiation from the source. The counter tube is surrounded by a thickness of 1.5 mm. of lead to eliminate soft γ -radiation. The α -particles fall on a target T of very thin lead or tin-foil. The dotted lines illustrate how γ -radiation from the foil may strike the counter.

The residual range of the α -particles striking the target was varied by regulating the pressure of air in the apparatus. A limit was set to the minimum amount of γ -radiation which could be detected by the large amount of γ -radiation produced by the incidence of β -rays on the target. We concluded that any γ -radiation produced by the α -rays is less than one quantum for 12,000 α -particles for a lead target, and less than one quantum for 20,000 α -particles for a tin target. The difference in the limit is due to the fact that tin-foil was available in thinner sheets than lead-foil.

No detailed investigation of the γ -radiation excited by the β -rays was made, but, since there seems to be very little published information on this subject ⁽⁷⁾, it may be of some value to record the approximate magnitudes of the effects observed.

From the geometry of the apparatus it is estimated that the fraction of all the α -particles and β -particles emitted by the source which strikes the target is about 0.03. Assuming that secondary γ -radiation from the target is emitted equally in all directions, the fraction of this which passes through the Geiger-Müller counter is about 0.005. The efficiency of the Geiger-Müller counter for detecting γ -radiation is, however, small—the number of discharges is only about 0.4 per cent. of the number of γ -ray quanta traversing the counter. Since an element of the radium series of 1 mg. radium equivalent emits 3.7×10^7 disintegration particles per

second, if each disintegration particle were effective in producing a secondary γ -ray quantum, then the number of discharges expected would be

$$3.7 \times 10^7 \times 60 \times 0.03 \times 0.005 \times 0.004 = 1350$$

per minute per mg. radium equivalent.

The natural effect of the counter, which was 10 cm. long \times 3 cm. diam., was about 25 discharges per minute. This may be ascribed mainly to cosmic radiation. In the absence of any target the scattered radiation entering the counter produced about 1.2 discharges per minute per mg. activity of the radium B+C source.

A thin tin-foil target of 8.8 mg./cm.² (about 3 cm. of air-stopping power) added about 1.6 discharges per min. per mg.

A target of thin lead-foil (52 mg./cm.²) yielded 7 per mg. per min. A thicker lead target (113 mg./cm.²) yielded about 15 per mg. per min.

We have seen that, if the observed number of discharges were 1350 per min. per mg., it would be concluded that one particle from each chain of disintegrations was effective in producing a γ -ray quantum. The observed number of discharges, 15 per min. per mg., therefore represents the production of a quantum of hard γ -radiation by about 1 per cent. of the β -rays. This estimate must, however, only be taken as indicating the order of magnitude of the effect, as there are important considerations which it is difficult to take into account. For example, there are β -rays from the disintegrations of both radium B and radium C spread over the energy range from about 1×10^5 to 2×10^6 electron volts. The minimum energy of β -rays which could excite γ -radiation detectable under the experimental conditions employed is not known with certainty, but is probably about 2×10^5 electron volts. Rough absorption measurements, however, showed that the observed γ -radiation had a mean energy of about 450,000 electron volts. It is therefore probable that the soft β -rays from radium B had very little effect. This is corroborated by an independent observation that the β -rays from radium E, which have a mean energy intermediate between those from radium B and radium C, excite much softer γ -radiation.

In contrast to the high yields obtained from lead and tin, a much smaller amount of secondary radiation

was observed from aluminium. A target of 29 mg./cm.² (about 19 cm. stopping power) produced about one discharge per min. per mg. This is explicable because large-angle deviation of a β -particle is more frequent in lead than in aluminium, and is in agreement with the results of J. A. Gray ⁽⁸⁾. This result is very similar to that of Slater, but it would be difficult to explain his observations as being due to β -particles, since high-energy β -rays are not known to accompany the radon-radium A transformation, and it would be necessary to postulate β -rays amounting to 1 per cent. of the α -particles. An experiment was made which showed that such β -rays do not occur in 1/10th of this amount.

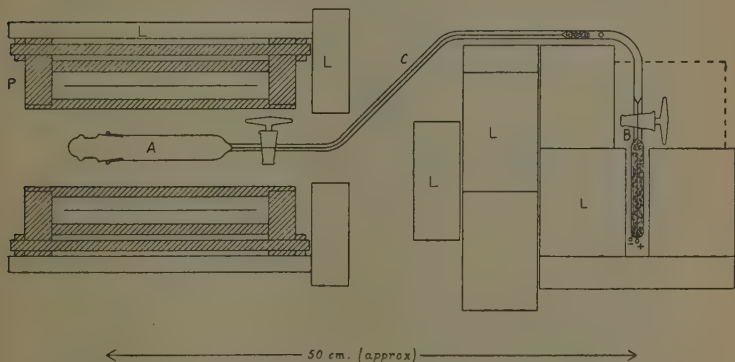
In our experiment a certain amount of the observed γ -radiation might possibly have been due to the annihilation in the target of positive electrons arising directly or indirectly from the source ⁽⁹⁾. It might also be expected that more of this annihilation radiation would be observed from a lead than from an aluminium target. It is not possible to explain Slater's results as due to the annihilation of positive electrons from the source, since his foils were always surrounded by a comparatively thick glass tube. Only very swift positive electrons could escape from this tube, the majority would be annihilated in the glass, and the amount of annihilation radiation would then be very much the same whether lead or paper lined the tube. If, on the other hand, it were suggested that positive electrons were formed in the lead target, then the primary radiation must be identified, and, as we have seen, there is no β -radiation, and α -particles give no appreciable effect.

THIRD EXPERIMENT.—*Annular Pressure Chamber.*

There still remained the possibility that the effect which Slater observed was due to some peculiarity of the radiations emitted by radon, and it was, therefore, decided to repeat Slater's experiment almost exactly. In his experiments radon was admitted to a tube lined with lead or paper, and the γ -ray activity of the tube was measured before an appreciable quantity of radium B+C had formed. We adopted the same principle, but with a modified apparatus (fig. 2). Measurements were made with an annular high-pressure ionization

chamber which had been used by L. H. Gray ⁽¹⁰⁾. This was connected to a Compton electrometer. A glass tube, A, exactly similar to that used by Slater, was placed in the central hole of the chamber. Emanation was admitted to the tube A from the bulb B through the capillary C. The ionization chamber, which was filled with nitrogen at about 30 atmospheres pressure, was screened from the γ -radiation from the active deposit in the bulb B by the lead blocks L, L. It was possible to obtain a measure of the γ -ray activity of the tube A within 10 seconds after opening the tap from the bulb B.

Fig. 2.



For the observation of the supposed effect this method of working should be a great improvement on that employed by Slater. Apart from the fact that he had only a lead electroscope for measurements of γ -ray activity, his method of sealing off and removing the tube B introduced a time-delay before starting measurements which wasted the time in which the most valuable observations would have been made. In our experiments the rate of drift of the Compton electrometer was followed continuously before and after opening the tap.

The annular pressure chamber conferred the advantage that, with a very moderate amount of lead screening, the natural leak was less than 1/20th of the minimum effect measured after opening the tap.

To determine the amount of radon introduced, the γ -ray activity due to the active deposit in the tube A was measured after about 40 minutes, when a reliable estimate of the final maximum activity could be obtained. The activity immediately after introducing the emanation was then expressed as a fraction of the maximum. The initial activity was consistently found to be $1/5000$ th of the maximum, and was the same whether the tube A was lined with lead or with paper, and was not affected by varying the amount of emanation (1 to 10 mg.), by drying the emanation for an hour with phosphorus pentoxide or by improving the filtering of the emanation by extra glass-wool or lead-foil plugs in the connecting tube close to the bulb B. The initial activity was always the same within 10 per cent. when expressed as a fraction of the maximum.

Slater reported that the initial activity in his experiments when paper lined the tube was less than $1/10,000$ th of the maximum, but when lead lined the tube the activity was $1/3000$ th of the maximum. These figures refer to measurements with comparable γ -ray absorption, namely, 5 mm. lead in his experiments and 8 mm. of iron in our experiments.

Conclusion.

These experiments raise difficulties in the way of interpreting Slater's results. It appears that the ionization which he observed cannot be attributed to γ -radiation excited by the α -particles, for all the other evidence shows that the amount of γ -radiation which is excited in heavy elements by the impact of α -particles is exceedingly small. The difference between the amounts excited in lead and in paper appears to be less than corresponds to one quantum of hard γ -radiation for 50,000 α -particles from radon. There is no evidence for the production of any γ -radiation from either lead or paper, even by the swifter α -particles from radium C', and no explanation has been found for Slater's experimental results.

A conceivable mechanism for the production of hard γ -radiation by α -particles is through the intermediate formation of pairs of positive and negative electrons. Each positive electron so formed gives rise subsequently

to annihilation radiation, which most frequently consists of two quanta of energy about 5×10^5 electron volts. The experiments may be interpreted as setting an upper limit for any such secondary production of γ -rays. From the first experiment, in which the annular magnet was used to separate the α -particles from the accompanying γ -radiation of the source, it is concluded that less than one pair of electrons is formed in lead by 10,000 α -particles from radium C'. The geometry of the second apparatus does not allow any definite estimate for such secondary processes. From the third experiment, with the annular pressure chamber, however, it may be concluded that the difference in the number of pairs produced when radon α -particles are stopped in lead and in paper is less than one pair for 100,000 α -particles.

Summary.

Attempts have been made in three ways to detect any hard γ -radiation produced by the impact of α -particles on tin or lead. The α -particles from radon and radium C' have been used. Slater, who worked with radon, had reported such γ -radiation. This was not confirmed, nor was any such radiation detected even with the much swifter α -particles from radium C'. These results are in agreement with those of Bothe and Becker, who used polonium α -particles. No explanation of Slater's observations has been found. It is concluded that any hard γ -radiation (5×10^5 electron volts) produced in lead must be less than one quantum for 12,000 α -particles from radium C', or less than one quantum for 50,000 α -particles from radon. The latter result depends on the assumption that an insignificant amount of hard γ -radiation is produced when the α -particles are stopped in paper.

The results may also be interpreted as setting an upper limit to any production of pairs of positive and negative electrons by α -particles. The conclusion is reached that radium C' α -particles produce in lead not more than one pair for 10,000 α -particles. Further, if it is assumed that no pairs are produced when the α -particles are stopped in paper, then it is also concluded that radon α -particles produce in lead not more than one pair for 100,000 α -particles.

In conclusion, we wish to thank Lord Rutherford and Dr. Chadwick for their interest in these experiments. We are also very indebted to Mr. D. E. Lea for his assistance with the pressure-chamber experiments and for putting at our disposal his Compton electrometer and other apparatus in working order. We must also thank Mr. G. R. Crowe for his assistance with some of the manipulation of the radium emanation. We are indebted to the Department of Scientific and Industrial Research and to the Goldsmiths' Company for their grants to enable us to carry out this work.

References.

- (1) Cockcroft and Walton, Proc. Roy. Soc. A, vol. cxxix. p. 477 (1930), and vol. cxxxvi. p. 619 (1932).
- (2) Bothe and Becker, *Z. Physik*, vol. lxvi. p. 289 (1930, and vol. lxxvi. p. 421 (1932).
- (3) Webster, Proc. Roy. Soc. A, vol. cxxxvi. p. 428 (1932).
- (4) Slater, Phil. Mag. vol. xlii. p. 904 (1921).
- (5) Lord Rutherford, Wynn-Williams, Lewis, and Bowden, Proc. Roy. Soc. A, vol. cxxxix. p. 617 (1933).
- (6) Cf. Kovarik, Phys. Rev. vol. xxiii. p. 559 (1924).
- (7) J. A. Gray, Proc. Roy. Soc. A, vol. lxxxv. p. 131 (1911), and vol. lxxxvi. p. 513 (1912); Chadwick, Phil. Mag. vol. xxiv. p. 594 (1912).
- (8) J. A. Gray, *loc. cit.*
- (9) Thibaud, 'Nature,' vol. cxxxii. p. 480 (1933); Chadwick, Blackett, and Occhialini, Proc. Roy. Soc. A, vol. cxliv. p. 235 (1934); Skobeltzyn and Stepanowa, 'Nature,' vol. cxxxiii. pp. 23, 565, 646 (1934).
- (10) L. H. Gray, Proc. Roy. Soc. A, vol. cxxx. p. 524 (1931).
- (11) L. H. Gray and G. T. P. Tarrant, Proc. Roy. Soc. A, vol. cxxxvi. p. 662, fig. 1 (1932).

XXII. *The Determination of Young's Modulus for Building Materials by a Vibration Method.* By G. GRIME, M.Sc.*

[Plate II].

ABSTRACT.

THE longitudinal vibration excited in a specimen by tapping one end is recorded photographically with the aid of a cathode-ray oscillograph, and its frequency is determined by comparison with a superimposed time-scale.

* Communicated by the Director of Building Research, Building Research Station, Garston, Herts.

Young's Modulus, E , is then calculated from the expression $E=4l^2n^2\rho$, connecting length l , frequency n , and density ρ .

INTRODUCTION.

MANY building materials are encountered in forms which make it difficult to determine Young's Modulus by the usual extensometer method. It is frequently possible, however, to obtain specimens suitable for the determination of the natural frequency of longitudinal vibration. Young's Modulus is then given by the expression ⁽¹⁾ .

$$E=4l^2n^2\rho/(1-\pi^2\sigma^2K^2/2l^2)^2,$$

where

E =Young's Modulus,

l =length of specimen,

n =frequency of longitudinal vibration,

ρ =density,

σ =Poisson's ratio,

K =radius of gyration of cross-section about the line of centres of the normal sections.

Specimens for frequency determination may generally be chosen, so that the bracketed term differs from unity by a negligible amount, when the first approximation,

$$E=4l^2n^2\rho,$$

is sufficiently accurate.

Methods described in the literature for determining the natural frequency fall into one of two classes, according as the measurement is made (1) by detecting the frequency at which resonance occurs when the specimen is maintained in forced vibration, or (2) by direct measurement of the frequency of vibration, set up by tapping or otherwise exciting the free vibrations of the specimen. The first method has been employed for measuring frequencies, velocities, and elastic constants by a number of investigators ⁽²⁾, the specimen being maintained in forced vibration by electrical means, generally either piezoelectric or magnetostrictive. The second includes the well-known experiments with rosined wires

and bars, excited by stroking, and an interesting investigation by Field ⁽³⁾ on vibrations in solid rods and disks, in which the vibrations were produced by repeated tapping and measured by comparison with a variable frequency oscillator. The arrangement described in this paper constitutes a simplified tapping method, recording photographically, on one trace, from a single tap, the data necessary for frequency determination.

EXPERIMENTAL.

The apparatus is shown diagrammatically in fig. 1.

Fig. 1.

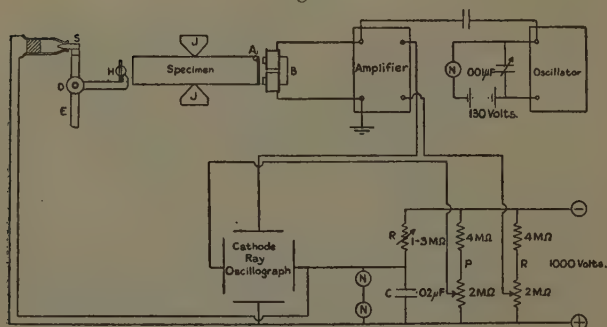


Diagram of Apparatus.

General Arrangement.

The specimen, in the form of a rod or cylinder of uniform cross-section, is held at the mid-point of its length and the free vibration is excited by a tap with a light hammer. An electromagnetic detector transforms the mechanical vibration into an electrical voltage oscillation which, after amplification, controls the vertical deflexion of the fluorescent spot of a cathode-ray oscillograph. A single-traverse time-base spreads out the vibration pattern horizontally across the screen at the correct moment, while a time-marker superimposes on the photographic record a break of very short duration every millisecond. The frequency is determined by comparison with that of the breaks.

Exciter and Detector.

Wooden jaws, J, fitted to a small vice hold the specimen firmly enough to prevent appreciable translatory motion when it is struck by the very light spring hammer, H. The position of the point of impact appears to be unimportant, but it is essential that the hammer shall be very light, in order that the duration of the blow shall be so short as to be comparable with the natural period.

The detector consists of a light soft iron armature, A, about $\frac{1}{32}$ in. thick, cemented to the end of the specimen, and separated by a small air-gap from a U-shaped permanent magnet, B, wound with coils of the type used in telephone receivers.

Amplifier.

The amplifier has to be capable of good response in the upper audible range, and for this purpose a resistance-capacity unit is most suitable, but as a direct-coupled amplifier of good characteristics was available from a previous investigation this has been used. The overall gain is 200, which has been found to furnish adequate sensitivity.

Cathode-ray Oscillograph and Time-base.

The oscillograph is normally operated at an anode voltage of from 600 to 1000, according to intensity requirements. Potentiometers, P, across the high-tension supply provide control of the initial position of the spot.

As there is no necessity for a linear time-base, a very simple type is used, consisting of a variable high resistance, R, and a condenser, C, whose plates are connected to the horizontally deflecting plates of the oscillograph in series, with the biasing voltage in the usual way. The condenser is charged from the oscillograph high-tension supply. When the apparatus is prepared for a record, the condenser is short-circuited by a switch, S, attached to the hammer-release, D, and the spot is deflected to the left-hand side of the screen. On releasing the hammer, by allowing a pendulum to strike the arm, E, the switch opens, and the voltage across the condenser rises, moving the spot horizontally across the screen at the correct moment to spread out the vibration pattern. At a voltage of approximately 300, when the spot has traversed the

screen, discharge takes place in two small neon lamps, N, connected in series across the condenser and, prevents any further voltage-rise.

The charging current, and with it the spot velocity, decrease exponentially as the condenser charges up. The rate of decrease is, however, quite small for the first part of the charging process, which is that used to move the spot across the screen. The time-base is, therefore, almost linear (see fig. 2 (a), Pl. II.).

Time-marker.

The registration of time-markings on the recording trace reduces the labour of interpreting records to a minimum. The time-marker is a development of one due to Richardson ⁽⁴⁾, but differs in that the voltage from the marker, instead of being applied to the focussing cylinder to unfocus the spot, is introduced into the amplifier to produce a vertical deflexion.

A neon lamp, N, and a battery of voltage just insufficient to cause flashing, are joined in series across the output of a fixed-frequency oscillator. With the oscillator working and the amplitude correctly adjusted, the neon lamp is flashed by one-half cycle and extinguished by the next, so that a surge of current takes place in the circuit once every cycle. Slight capacitative coupling with the input of the amplifier is sufficient to superimpose this on the record as a short-duration impulsive deflexion recurring at regular intervals. A condenser across the output of the oscillator gives some control of the shape and duration of the impulse. Fig. 2 (a) (Pl. II.) is a record of the time-marking. The impulse has a duration of approximately 50 microseconds, and occurs 1024 times per second.

The frequency of the time-marker has been checked over a period of months against a 1024 fork by superimposing the time marks on the record obtained from the fork. The frequency was found to remain constant within 0.25 per cent. over the period of the observations.

Camera.

With a Ross Xpres f. 1.9 lens fitted to a quarter-plate camera, records of frequencies up to 15,000 per second may be made without recourse to highly sensitive plates.

Half a dozen records are taken on each plate by traversing the plate-holder vertically.

Density Determination.

Measurements of length and density require no description. It should be noted, however, that for dry porous materials the appropriate density is the bulk density. Wet porous materials have not been dealt with up to the present, as the part played by the water in the pores in transmitting vibration is not known.

Accuracy.

The length of an average specimen—approximately 7 in.—can be measured with an error of less than 0.3 per cent., and the density can be determined within 0.3 per cent. The frequency of vibration can readily be measured within 0.5 per cent. The possible error of a determination, is therefore, 2.1 per cent. Greater accuracy in the measurement of frequency could be obtained by making a longer record on moving film, but, in view of the variability of the materials investigated, the sacrifice of simplicity consequent upon this change is hardly justified by the slight increase in accuracy.

Results.

Fig. 2 (b) (Pl. II.) is the record of the free longitudinal vibration of a specimen of asbestos cement sheeting 7 in. long by 1 in. wide by 0.2 in. thick. The breaks due to the time marker are clearly seen. The natural frequency is 9450 per second, and the density is 2.01, which gives Young's Modulus $E=3.2$ million lb. per sq. in.

A comparison of the vibration method with the usual extensometer method has been made for a circular steel bar 18 in. long by 0.5 in. in diameter. Fig. 2 (c) (Pl. II.) is the vibration record. The natural frequency is 5650 per second, giving $E=30.0 \pm 0.4$ million lb. per sq. in., in good agreement with the value 30.4 ± 0.3 million lb. per sq. in. obtained by the extensometer method.

APPLICATIONS OF THE METHOD.

Materials for which Young's Modulus has been determined include stone prisms of triangular cross-section,

roofing tiles, asbestos-cement sheeting, bricks of rectangular and circular cross-section, and lime mortars of very low strength. The apparatus provides a very convenient means of observing progressive changes in Young's Modulus—for example, those due to heat treatment or to weathering—and, as large numbers of small specimens may be dealt with rapidly, comparisons are possible on a statistical basis.

REFERENCES.

- (1) Love, A. E. H., 'The Mathematical Theory of Elasticity,' 4th ed. p. 290. Cambridge University Press, 1927.
 - (2) Quimby, S. L., *Phys. Rev.* xxv. pp. 558-73 (1925); Pierce, G. W., *Proc. Am. Acad. Sci.* lxiii. pp. 1-47 (1928); Muzzey, D. S., *Phys. Rev.* xxxvi. pp. 935-47 (1930); Boyle, R. W., and Sproule, D. S., *Can. J. Research*, v. pp. 601-18 (1931); Zacharias, J., *Phys. Rev.* xlv. pp. 116-22 (1933); Giebe, E., and Blechschmidt, E., *Ann. d. Physik*, (4) xviii. pp. 417-56 (1933); (5) pp. 457-85.
 - (3) Field, G. S., *Can. J. Research*, viii. pp. 563-74 (1933).
 - (4) Richardson, L. F., *Proc. Phys. Soc. Lond.* xlv. pp. 135-41 (1933).
- Garston, March 1935.

XXIII. *Constitution of Water in Solutions of Weak Electrolytes.—I. Formic and Acetic Acids.* By C. S. SIVA RAO, M.A., *Andhra University, Waltair (India)* *.

1. Introduction.

FROM the standpoint of dissociation, as much work was done on weak electrolytes as on strong electrolytes. The phenomena of electrolytic conductivity, osmotic pressure, and related effects, etc., have all been very satisfactorily accounted for in the case of solutions of weak electrolytes. In fact, all the theories of electrolytic dissociation, excepting the one recently put forth by Debye and Hückel, accounted only for observations with solutions of weak electrolytes in water, but failed when applied to strong electrolytes. The work on the other aspect of the problem, namely, the influence of dissolved substances on the behaviour of the solvent,

* Communicated by Prof. I. R. Rao, M.A., Ph.D., D.Sc. (Lond.).

is, however, very meagre for weak electrolytes. Although there have been attempts in this direction by a study of the structure of the Raman band in solutions of strong electrolytes in water, the other characteristic groups of substances—weak and non-electrolytes—have not been thus far investigated by this means, and the author has, therefore, sought to work with some typical substances of these two classes also.

In the case of many strong electrolytes it was found, as could be seen from the previous work of the author *, that the ions into which the electrolytes are dissociated form molecular complexes due to combination with the molecules of the solvent—a phenomenon known as solvation in general, or hydration in the particular case of water used as solvent. But, in the case of weak electrolytes, not much work seems to have been done on this aspect of the nature of solution. Jones and Getman † worked with a few organic acids with a view to study the presence of hydration in their aqueous solutions and arrived at the conclusion that they exhibited little tendency to form hydrates.

Krishnamurti ‡ worked with solutions of acetic acid in water at different concentrations with the idea of studying the changes noticeable in its Raman lines. He found that a new line at 1707 cm.^{-1} appeared at about 95 per cent. concentration of the acid, in addition to the line at 1667 cm.^{-1} present in the pure acid. He observed that this line increased in intensity with further dilution till it was the only line present at 75 per cent. and lower concentrations. He attributed this to the formation of the monohydrate, $\text{CH}_3\text{COOH} \cdot \text{H}_2\text{O}$ (77 per cent. acid), and pointed out that this result is in agreement with that obtained from the density curves for acetic acid solutions, which show a maximum at 77 per cent. (25° C.) concentration of the acid, which is doubtless due to the formation of a hydrate.

Formic acid is also known to form hydrates§, in particular the hydrate represented by $4\text{HCOOH} \cdot 3\text{H}_2\text{O}$, which at 107.1° C. dissociates into formic acid and water,

Having worked with solutions of strong electrolytes,

* 'Indian Journal of Physics,' vol. ix. p. 195 (1934).

† Publication No. 60 of the Carnegie Institution of Washington (1907).

‡ Ind. Journ. Phys. vol. vi. p. 401 (1931).

§ Richter's 'Organic Chemistry,' vol. i. p. 237.

the study of which has been described in a previous communication*, it is now proposed to describe and discuss the results obtained with weak electrolytes as influencing the constitution of water when they are dissolved in it.

2. Experimental Details.

The one great handicap attendant on the work on the Raman effect in solutions of highly soluble weak electrolytes, as compared with that on strong electrolytes, is the trouble due to the presence of a large amount of continuous background in their Raman spectra, which makes it well-nigh impossible to obtain any trustworthy results with them. Even with two or three slow redistillations of the liquids to be investigated, and with all the usual light-filters tried, the presence of the continuous spectrum was still very considerable. Therefore, only formic and acetic acids could be so far studied in their aqueous solutions with a view to investigate the structure of their Raman water-band.

The experimental arrangement employed in these investigations is that described in a previous communication†. The light-filter used in the present case is a solution of chromium sesquichloride, which is found to very appreciably cut off the continuous spectrum in the position of the band excited by the 3650 λ group of mercury lines. This filter freely transmits the 3650 λ group, but effectively absorbs the 4047 λ and 4358 λ lines, so that excitation by the former is used. This has an incidental advantage in that the Raman lines present in the scattered spectra of the acids and excited by the 4047 λ line, which otherwise get superposed on the band excited by the 3650 λ group, are suppressed in the present case owing to the effective absorption of the exciting line itself by the filtering liquid. The mercury lamp is run under low intensity and the liquid under investigation is cooled during the course of an exposure by circulation of running cold water.

3. Results.

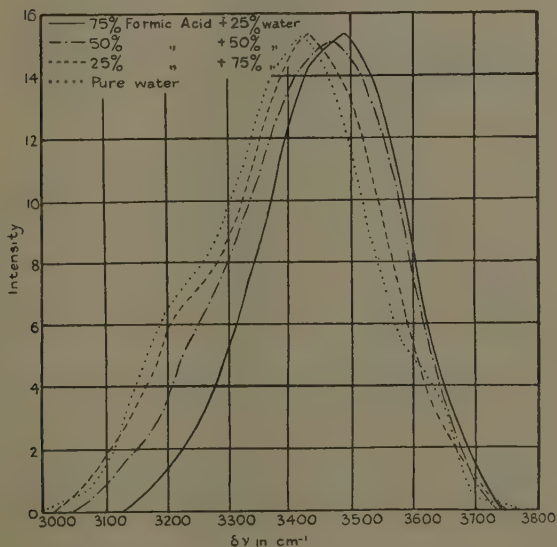
Fig. 1 represents the intensity curves of the Raman water-band excited by the 3650 λ group in 75, 50, and

* *Loc. cit.*

† I. Ramakrishna Rao and C. Sambasiva Rao, *Zeits. f. Phys.* vol. lxxxviii. p. 127 (1934).

25 per cent. (by volume) solutions of formic acid, together with the curve for pure water, which is given for purposes of comparison (fig. 1). All of them are studied at the laboratory temperature, viz., 31° C. The distribution of intensity along the band in pure water and in the three solutions is given in Table I. (p. 314).

Fig. 1.



Intensity distribution along the Raman water-band in solutions of formic acid at different concentrations and pure water.

From a study of the intensity curves the following results are obvious :—

(i.) The band gets sharper with increasing concentration of the acid.

(ii.) There is a progressive shift in the maximum of the band, as well as of the band as a whole, towards the side of larger frequency with increasing concentration.

(iii.) The smaller frequency portion of the intensity curve, which is decidedly convex at the smallest concentration studied, viz., 25 per cent. acid and 75 per cent.

water, becomes less convex at the next higher concentration, 50 per cent. acid, and is unmistakably concave in its shape at the highest concentration, 75 per cent. acid.

In fig. 2 are represented the intensity curves of the Raman water-band for pure water and 75, 50 and 25 per cent. solutions of acetic acid in water (fig. 2). The

TABLE I.

Intensity Distribution along the Raman Water-band in the Pure Solvent and Solutions of Formic Acid.

Pure water.		Formic acid.					
		75 per cent.		50 per cent.		25 per cent.	
$\delta\nu$ in cm. ⁻¹ .	Intensity.	$\delta\nu$ in cm. ⁻¹ .	Intensity.	$\delta\nu$ in cm. ⁻¹ .	Intensity.	$\delta\nu$ in cm. ⁻¹ .	Intensity.
3013	0.15	3175	0.93	3111	1.18	3051	0.54
3063	0.54	3245	2.64	3220	4.81	3111	2.12
3157	4.59	3304	5.97	3330	9.85	3172	4.28
3233	7.42	3373	10.59	3375	12.43	3204	5.94
3300	9.94	3426	14.22	3438	14.64	3271	7.63
3360	13.65	3458	14.90	3471	15.00	3343	11.50
3403	14.90	3492	15.27	3497	14.55	3396	14.53
3435	15.00	3537	13.87	3569	10.75	3448	15.00
3503	10.97	3579	9.98	3613	6.42	3495	13.30
3568	5.91	3647	3.98	3651	2.98	3569	7.48
3627	3.96	3689	1.56	3705	0.59	3633	3.01
3689	0.53	—	—	—	—	3705	0.75

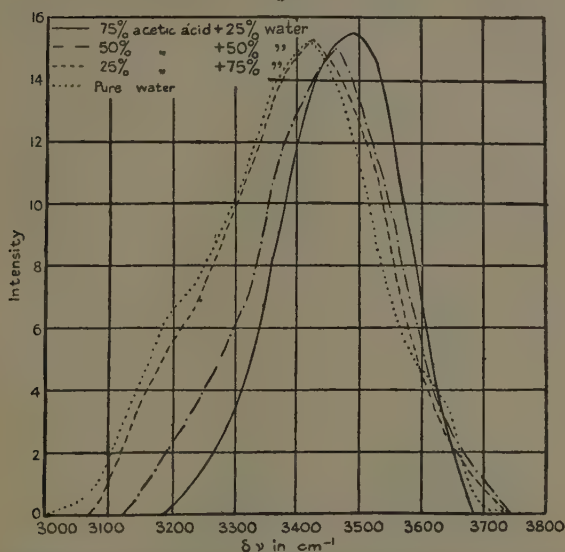
distribution of intensity along the band in the above cases is contained in Table I., given above, and Table II. (p. 315).

Results very similar to those obtained above in the case of formic acid have been obtained with increasing concentration of acetic acid also.

Table III. (p. 316) shows the positions of the intensity maximum of the water-band in solutions of formic and acetic acids at the three different concentrations studied.

Having worked with solutions of each of the acids under different concentrations, it was thought desirable, for a better understanding of the problem, to compare

Fig. 2.



Intensity distribution along the Raman water-band in aqueous solutions of acetic acid at different concentrations and pure water.

TABLE II.

Intensity Distribution along the Raman Water-band in Solutions of Acetic acid at Different Concentrations.

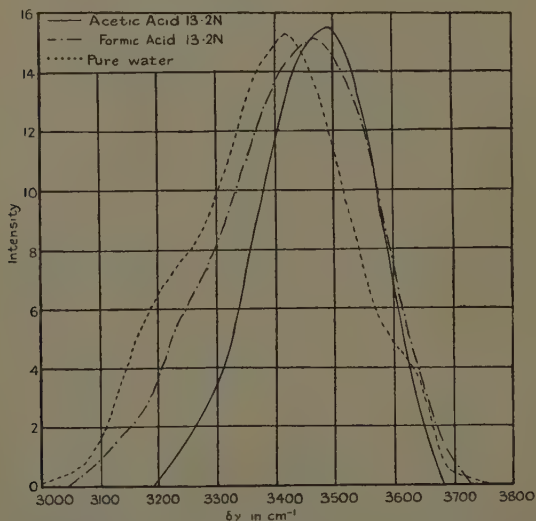
75 per cent. acid.		50 per cent. acid.		25 per cent. acid.	
$\delta\nu$ in cm. ⁻¹ .	Inten- sity.	$\delta\nu$ in cm. ⁻¹ .	Inten- sity.	$\delta\nu$ in cm. ⁻¹ .	Inten- sity.
3268	1.94	3176	1.52	3107	1.50
3308	3.67	3268	4.66	3172	4.44
3350	7.32	3320	6.95	3229	6.34
3384	10.32	3366	11.56	3279	8.72
3435	14.53	3418	13.46	3353	12.56
3480	15.40	3463	15.00	3395	15.17
3526	14.97	3507	12.81	3435	15.00
3560	10.92	3551	9.79	3477	13.87
3606	6.06	3639	3.00	3533	10.74
3650	1.96	3686	1.42	3591	5.03
—	—	—	—	3652	2.09

the results obtained for the two substances under conditions that readily permit of a reliable comparison. The acids were, therefore, next studied under the same

TABLE III.

Substance.	Concentration.	Position of intensity maximum.
1. Water	3424 cm. ⁻¹
2. Formic acid	25 per cent. (by volume).	3434 "
" "	50 " " "	3467 "
" "	75 " " "	3487 "
3. Acetic acid	25 " " "	3427 "
" "	50 " " "	3463 "
" "	75 " " "	3483 "

Fig. 3.



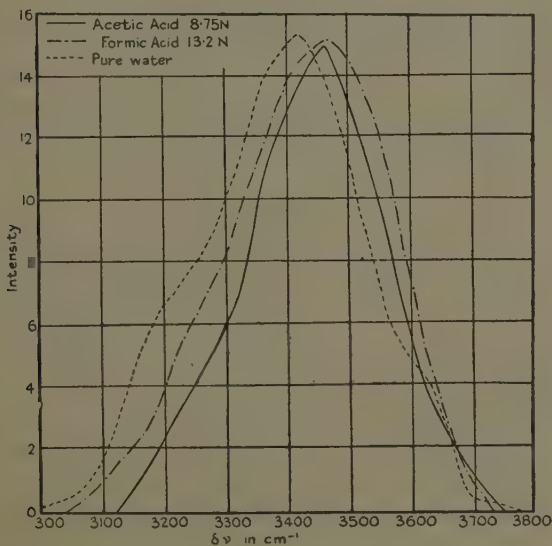
Intensity distribution along the Raman water-band in formic and acetic acids at the same concentration, 13.2 N, and pure water.

molal concentration, so that the same number of molecules of the dissolved weak electrolyte are influenced by those of the solvent in each case. Fig. 3 gives the intensity

curves of the Raman band for water in solutions of formic and acetic acids having the same molal concentration, viz., 13.2 N. It will be seen from the above figure that, at the same concentration, the curve for acetic acid is much sharper than and shifted to the side of greater frequency with respect to the curve for the solution of formic acid.

Such a study as the above gives an idea of the characteristic influence of each of the dissolved substances

Fig. 4.



Intensity distribution along the Raman water-band in solutions of formic and acetic acid at the same water-content and pure water.

individually and as compared with one another. The influence of the dissolved weak electrolyte may result, as with the strong electrolytes studied before, in either of the two following changes: (a) there may be hydration of the molecules of the dissolved substance due to association with those of the solvent; (b) there may be produced a change in the water equilibrium between the proportions of the single, double, and triple molecules assumed to

exist in liquid water. If the effect of the dissolved substance is mainly to bring about a change in the water equilibrium, and is not affected by its nature and constitution, then, when the amount of water contained in a definite volume of the solution is equalized for each of the substances investigated, so that the molecules of the solute are influenced by the same number of molecules of the solvent in each case, the results obtained would be independent of the nature of the dissolved substance, and the Raman band for water would be identical in its structure in all of them. To examine whether such an effect is present, the intensity distribution along the water-band in solutions of the two acids is next compared with the water-content in them equalized, and the intensity curves of the water-band thus obtained in solutions of the two acids containing the same water-content as 13.2 N concentration of formic acid are represented in fig. 4. The concentration of

TABLE IV.

Solution.	Position of intensity maximum.	
	At the same concentration.	At the same water-content.
1. Water	3424 cm. ⁻¹	3424 cm. ⁻¹
2. Formic acid, 13.2 N	3467 „	—
Acetic acid, 13.2 N	3483 „	—
3. Formic acid, 13.2 N	—	3467 „
Acetic acid, 8.75 N	—	3463 „

acetic acid having this water-content is 8.75 N. Similar to the results observed with solutions of strong electrolytes at the same concentration and at the same water-content, in the present case also, when the quantity of water contained in the same volume of solution of each of the acids is equalized, the differences noticed above at the same concentration of the acids get reduced, the curves tending to become similar.

In Table IV. are set forth the positions of the intensity maximum of the water-band in solutions of acetic and formic acids at the same concentration and at the same water-content.

The following is a generalized summary of the results obtained from a study of the two weak electrolytes investigated here :—

(i.) The Raman band for water gets sharper and shifts to larger frequency with increasing concentration of the dissolved substance.

(ii.) The smaller frequency branch of the intensity curve of the water-band changes from convex to concave in its shape as the concentration of the solute is increased.

(iii.) The water-band for acetic acid is sharper than and shifted to greater frequency with respect to that for formic acid at the same concentration, but, when their water-content is equalized, these differences tend to get minimized.

4. Discussion.

The results obtained with increasing concentration of formic and acetic acids are similar to those observed in the case of strong electrolytes *, with the exception of solutions of hydrochloric acid and chlorides, and discussed in detail in that connexion. The changes noticed in the structure of the water-band with increasing addition of the weak electrolytes may, therefore, arise, as with the strong electrolytes, out of a change in the water equilibrium due to variation in the proportions of the single (H_2O), double (H_2O)₂, and triple (H_2O)₃ molecules supposed to exist in liquid water, as well as out of a change in hydration of the molecules of the dissolved substance. It has been pointed out elsewhere † that the effect of a change in hydration on the structure of the Raman water-band is similar to the effect of variation in the proportions of the three types of water-molecules, and that, so far, it has not been possible to clearly distinguish between the two effects.

Thus, the observed results of an increasing sharpness in the band, a shift towards greater frequency, and a gradual change from a decisive convexity to a pronounced concavity in the shape of the smaller frequency branch of the intensity curve with increasing concentration of the

* *Loc. cit.*

† C. S. Siva Rao, "Effect of a Change in Temperature on the Constitution of Water in Solutions of Electrolytes," *Proc. Roy. Soc. Lond.* (in press).

dissolved substance—all point to the conclusion that increasing addition of the weak electrolyte, in both the cases studied, causes a decrease in the proportion of the most complex molecules, viz., trihydrol (H_2O)₃, with a simultaneous increase in that of the single molecules of the type (H_2O), while the proportion of the double or the so-called "water"-molecules does not vary appreciably. Also, the more complex hydrates get dissociated into simpler hydrates and single water-molecules at the higher concentrations of the acids studied. It is not possible to clearly distinguish what part of the observed effect originates in each of the causes noted above, as each produces the same results and causes the same variations in the structure of the Raman band for water.

If, as was noted by Jones and his co-workers*, there is no appreciable hydration taking place in aqueous solutions of these organic acids, then the observed results are to be mainly attributed to an alteration in the proportions of mono-, di-, and trihydrol with change of concentration of the dissolved substance; but, the magnitude of the observed changes is at least as considerable as that noticed in the case of strong electrolytes, and the changes are, perhaps, even more prominent in the present case. It would, therefore, seem probable that the same causes as were noticed to be present in the case of strong electrolytes studied before are operative in the case of the weak electrolytes studied here, and that the observed results are not altogether due to a mere change in the water equilibrium.

Considering next the results obtained from figs. 3 and 4 for the two acids at the same concentration and at the same water-content, the fact that the intensity curve of the water-band for acetic acid at 13.2 N concentration is much sharper than, and shifted to the side of larger frequency with respect to, the curve for formic acid at the same concentration points to the conclusion that the proportion of the more complex water-molecules and hydrates is relatively greater in formic acid than in acetic acid at the same molal concentration. Further, the fact that, when the water-content in solutions of the two acids is equalized, the differences noticed at the same concentration get minimized and the band for

* *Loc. cit.*

acetic acid tends to become similar to that for formic acid, the maxima of intensity in the two cases very nearly coinciding, shows that a shift in the water equilibrium, due to a change in the proportions of the triple, double, and single water-molecules is, at least in part, the cause of the observed results. Nevertheless, there are still observable certain differences in shape and sharpness of the intensity curves of the water-band at the same water-content of the acids, which can only be explained as arising out of a difference either in the extent of the change in water equilibrium, or in hydration between the two acids studied, or, what is more probable, to the simultaneous presence of both the factors. The results discussed here in relation to weak electrolytes are very similar to those recorded before for solutions of strong electrolytes in water.

Thus the two acids—formic and acetic—studied so far, and belonging to the class of substances known as weak electrolytes, appear to behave in their aqueous solutions in a manner exactly analogous to that of strong electrolytes, and further work alone with more substances of this group will make it clear whether weak electrolytes behave as a class by themselves or in a manner similar to strong electrolytes as regards their influence on the constitution of water in their aqueous solutions.

In conclusion, the author desires to express his grateful thanks to Dr. I. Ramakrishna Rao for his kind advice and interest throughout the progress of the above investigation.

5. *Summary.*

The constitution of water in solutions of the two weak electrolytes, formic and acetic acids, is investigated by a study of the structure of the Raman band for water in them. The main results obtained are :—

(a) The water-band gets sharper and shifts to larger frequency with increasing concentration of the dissolved substance, the smaller frequency branch of its intensity curve at the same time changing from convex to concave in its form.

(b) When studied at the same concentration, the band in acetic acid solution is sharper than, and shifted to

the side of greater frequency as compared with, that for the solution of formic acid ; but, when the water-content in the two solutions is equalized, these differences are less conspicuous.

The above results are discussed in relation to change in water equilibrium and hydration, and the close similarity between the results herein obtained and those observed with solutions of strong electrolytes studied before is pointed out.

Andhra University College of
Science and Technology, Waltair.
January 1935.

XXIV. *Some Solutions of the Problem of Forced Convection.*

By W. G. BICKLEY, D.Sc., Imperial College of Science and Technology.*

1. *Introduction.*

THE problem of forced convection—the transport of heat from a hot solid by a stream of relatively cool fluid—has from time to time received attention by various mathematical physicists. Despite the evident practical importance of the problem, it cannot be said that our knowledge of it is yet, especially from a theoretical standpoint, at all complete. The most general problem, where the shape of the solid is not simple, and when the viscosity, thermal expansion, and compressibility of the fluid, and the temperature variations of these and of the specific heat, are taken into account, presents very considerable difficulties. In the present state of our knowledge, however, exact solutions of the idealised problem, in which the fluid is assumed to be inviscid and incompressible, its motion irrotational, and its physical properties independent of temperature, would seem to be of value, and are certainly of interest.

The first considerable progress would seem to have been made by Boussinesq ⁽¹⁾, to whom is due the transformation of the differential equation for the two-dimensional case into a simple standard form, by the use of the velocity

* Communicated by the Author.

potential and stream function as coordinates. He did not, however, use the exact form of this differential equation, but removed one term, a term whose effects are admittedly, in certain circumstances, small. Russell⁽²⁾ gave an account of earlier work, and solved a few more cases, using Boussinesq's "reduced" equation. H. A. Wilson⁽³⁾ gave the solution of the complete equation representing a line-source in a stream. Further progress was made by King⁽⁴⁾, who used Wilson's solution in an attempt to improve Boussinesq's result for the heat loss from a circular cylinder. (King also did a considerable amount of experimental work on the cooling of heated wires, with a view to improving the accuracy of hot wire anemometry. He used the results of his theoretical investigations in reducing his experimental results, but his final formula is, at least in part, empirical.) Although King, in his theory, used the exact differential equation, his boundary conditions were artificial, and have been criticised at length by Piercy and Winny⁽⁵⁾. These last writers use approximations to the solution of the differential equation, but correct boundary conditions, and obtain results agreeing tolerably well with King's and other experiments.

Zeilon⁽⁶⁾, and Southwell and Squire⁽⁷⁾, in applying a modification of Oseen's method of approximation to the motion of a viscous fluid, encounter the same differential equation. The last-named writers, starting with what is essentially Wilson's solution, and using numerical and graphical methods of integrating the fundamental "point source" solution to satisfy approximately the conditions along an extended boundary, obtain a number of interesting and valuable results. Their boundary conditions, however, naturally differ from those appropriate to the convection problem.

In all the above work, mathematical approximations (in addition to simplified physical assumptions) were made, and, so far as the author is aware, mathematically accurate solutions of the complete differential equation satisfying the condition that the temperatures of the solid and of the fluid immediately in contact with it are at all points equal, have not previously been given. The present paper is devoted mainly to three such solutions for simple distributions of temperature or heat emission along the boundary, and to the comparison of these with previous

work. It is therefore predominantly mathematical in character.

2. Fundamental Equations.

We commence with a résumé of the fundamental equations of the problem.

Consider a stream of incompressible inviscid fluid, of constant heat conductivity k and heat capacity c per unit volume; let (u, v, w) denote the velocity components at any point (x, y, z) in the directions of mutually perpendicular axes. Then, if τ denote the temperature of the fluid, the rate of increase of the heat content of the element $dx dy dz$ will be

(a) $k \nabla^2 \tau dx dy dz$, due to conduction,

(b) $-c(u \partial \tau / \partial x + v \partial \tau / \partial y + w \partial \tau / \partial z)$, due to convection.

Equating the sum of these to the time rate of change of the heat content of the element, we obtain

$$k \nabla^2 \tau - c \left(u \frac{\partial \tau}{\partial x} + v \frac{\partial \tau}{\partial y} + w \frac{\partial \tau}{\partial z} \right) = c \frac{\partial \tau}{\partial t}, \quad (2.1)$$

t denoting time. When the steady state has been reached, so that $\partial \tau / \partial t = 0$, the equation satisfied by the temperature is

$$\nabla^2 \tau = \frac{c}{k} \left(u \frac{\partial \tau}{\partial x} + v \frac{\partial \tau}{\partial y} + w \frac{\partial \tau}{\partial z} \right). \quad (2.2)$$

If the fluid motion is irrotational, and only two-dimensional, u and v are given in terms of a velocity potential ϕ and an associated stream function ψ by the usual equations

$$u = -\partial \phi / \partial x = -\partial \psi / \partial y, \quad v = -\partial \phi / \partial y = \partial \psi / \partial x,$$

and the transformation to ϕ and ψ as independent variables reduces (2.2) to the canonical form

$$\frac{\partial^2 \tau}{\partial \phi^2} + \frac{\partial^2 \tau}{\partial \psi^2} + \frac{c}{k} \frac{\partial \tau}{\partial \phi} = 0, \quad (2.31)$$

which is Boussinesq's equation.

It follows from this that all two-dimensional cases of flow past an obstacle can be transformed into that of a uniform stream flowing past a plane whose trace is the linear transformed contour of the obstacle, conveniently taken as a portion of the ϕ -axis. If U is the velocity

of the original stream at infinity, it is convenient to revert to variables X, Y , given by $\phi = -UX$, $\psi = -UY$, giving

$$\frac{\partial^2 \tau}{\partial X^2} + \frac{\partial^2 \tau}{\partial Y^2} = \frac{cU}{k} \frac{\partial \tau}{\partial X} \quad \dots \quad (2.32)$$

It is evidently possible to reduce this equation to a non-dimensional form; in doing so, it is convenient, for further developments, to have a factor 2 in the coefficient of $\partial \tau / \partial X$, so we write $cU/k = 2n$, $\alpha = nX$, and $\beta = nY$. The resulting equation is

$$\frac{\partial^2 \tau}{\partial \alpha^2} + \frac{\partial^2 \tau}{\partial \beta^2} = 2 \frac{\partial \tau}{\partial \alpha} \quad \dots \quad (2.4)$$

Boussinesq omitted the term $\partial^2 \tau / \partial \alpha^2$, as being small, and used Fourier's solution of the "reduced" equation for a given temperature distribution along the α -axis.

The general solution of the equation (2.4) can be found by use of the substitution $\tau = T e^\alpha$, for the equation for T is then

$$\frac{\partial^2 T}{\partial \alpha^2} + \frac{\partial^2 T}{\partial \beta^2} = T, \quad \dots \quad (2.5)$$

the typical solution of which, in terms of polar coordinates (ρ, θ) corresponding to the rectangular coordinates (α, β) , even in θ , and vanishing at infinity, is

$$T = K_n(\rho) \cos n\theta,$$

K_n denoting the Bessel function of "imaginary argument" as defined in Watson's 'Bessel Functions.' The symmetrical solution,

$$\left. \begin{aligned} T_0 &= K_0(\rho) \\ \tau_0 &= e^\alpha K_0(\rho) \end{aligned} \right\}, \quad \dots \quad (2.6)$$

is evidently appropriate to a line-source at the origin, and Wilson showed that the formula for a line-source of strength Q per unit length is

$$\tau_0 = \frac{Q}{2\pi k} e^\alpha K_0(\rho), \quad \dots \quad (2.62)$$

Before proceeding further, the boundary conditions must be considered. In the absence of any information to the contrary, we will take it that the temperature of the fluid in contact with the solid is equal to that of the solid.

Problems then fall into two main classes: (a) determination of temperature due to given heat emission from the surface of the solid, and (b) determination of heat emission due to given temperature distribution on the surface of the solid. Of these, class (a) will be approximated to in practice when the solid is a poor conductor, supplied with heating elements, as in the common electrical heating elements. Class (b) will occur when the solid is a good conductor, such as a metal pipe carrying steam, and in this case the temperature will be approximately constant over the surface.

The heat loss from the solid in case (b) can be calculated when the temperature distribution in the fluid near the solid has been found. If ds is an element of the trace of the solid, and dn an element of the normal, drawn into the fluid, the rate of heat loss across ds , per unit length of the solid, is $-k(\partial\tau/\partial n).ds$. When we transform to variables (α, β) , we have $ds=J d\alpha$ and $dn=J d\beta$, where J is given by $J^2=(\partial x/\partial\alpha)^2+(\partial y/\partial\alpha)^2$, so that the heat loss is $-k(\partial\tau/\partial\beta).d\alpha$. It follows that the heat loss over any portion of the boundary is equal to that over the corresponding portion of the plane whose trace is the α -axis in the transformed problem. (It does *not* follow, however, that the heat loss per unit *length* of contour is equal to the heat loss per unit length of the α -axis at the corresponding point—these are in the ratio 1:J.) This last result makes it possible to transform problems of class (a), *i. e.*, to determine the boundary value of $\partial\tau/\partial\beta$ that the appropriate solution of (2.4) must have.

If, in either class of problem, the heat emission on one side of the α -axis for an element $d\alpha$ is $q(\alpha) d\alpha$ (per unit length of generator), this is equivalent to a distribution of sources of the type (2.62) with line density $2q(\alpha)$, so that the temperature at any point of the (α, β) plane is given by

$$\pi k\tau = \int q(\alpha') e^{\alpha-\alpha'} K_0(\rho') d\alpha', \quad \text{.} \quad (2.7)$$

where $\rho'^2 = (\alpha - \alpha')^2 + \beta^2$,

and the solution of any problem of class (a) is reduced to the evaluation of this integral, provided, of course, the requisite transformation formula connecting $(\alpha + i\beta)$ and $(x + iy)$ is known. For problems of class (b), putting $\beta=0$ in (2.7) yields an integral equation for $q(\alpha)$. No general formal solution of this integral equation seems

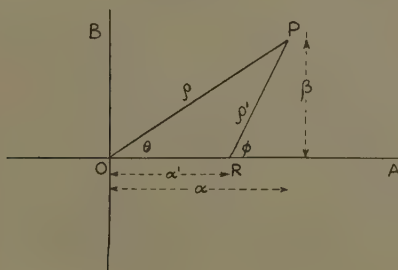
to have been given, although Piercy and Winny have obtained approximate solutions by using approximations to K_0 . In the next section, a solution of this integral equation, when the temperature is prescribed over the whole α -axis, from $-\infty$ to $+\infty$, will be constructed,—actually from the solution of a much simpler integral equation.

3. Temperature prescribed along the α -axis.

A solution of (2.4) having properties which make it a useful starting-point is the function

$$\tau_{\frac{1}{2}} = e^{\alpha} K_{\frac{1}{2}}(\rho) \cos \frac{1}{2}\theta = \sqrt{(\pi/2\rho)} \cdot e^{\alpha-\rho} \cos \frac{1}{2}\theta. \quad (3.1)$$

Fig. 1.



This is evidently zero when $\theta = \pi$, and reduces to $\pm(\pi/2\rho)$ when $\theta = 0$. It is, unfortunately, not single-valued, so that the solutions derived from it are valid over a half-plane only.

Suppose line-sources giving rise to (3.1) are distributed along the positive half of the α -axis with line-density $f(\alpha)$. Then, if P is any point in the upper half-plane, R the point $(\alpha', 0)$, $RP = \rho'$, and the angle made with the positive direction of the α -axis by RP is ϕ (see fig. 1), the temperature at P will be

$$\tau = \int_0^{\infty} e^{\alpha-\alpha'} K_{\frac{1}{2}}(\rho') \cos \frac{1}{2}\phi f(\alpha') d\alpha'. \quad (3.2)$$

By what has been said, it is evident that τ will be zero along the negative portion of the α -axis, and along the positive portion, the value at the point $(\alpha, 0)$ will receive

no contribution for values of $\alpha' > \alpha$. Consequently, the value of τ at this point will be

$$\tau(\alpha, 0) = \sqrt{\frac{\pi}{2}} \int_0^\alpha \frac{f(\alpha') d\alpha'}{\sqrt{(\alpha - \alpha')}}. \quad (3.31)$$

This is an integral equation (Abel's) for $f(\alpha')$, when $\tau(\alpha, 0)$ is known. It is sufficient for the moment to obtain the solution for the special case $\tau = \text{const.}$, and the constant can be taken as unity without any real loss of generality. Putting $\tau = 1$, and $\alpha' = \alpha u$, we have

$$1 = \sqrt{\frac{\pi}{2}} \int_0^1 \frac{f(\alpha u) \alpha^{\frac{1}{2}} du}{\sqrt{(1-u)}}. \quad (3.32)$$

A solution is obviously $f(\alpha u) = C(\alpha u)^{-\frac{1}{2}}$, when C is given by

$$1 = C \sqrt{\frac{\pi}{2}} \int_0^1 u^{-\frac{1}{2}} (1-u)^{-\frac{1}{2}} du = \pi^{\frac{1}{2}} 2^{-\frac{1}{2}} C,$$

so that

$$C = 2^{\frac{1}{2}} \pi^{-\frac{1}{2}}.$$

Consequently,

$$\begin{aligned} \tau_2 &= \sqrt{\frac{2}{\pi^3}} \int_0^\infty e^{\alpha - \alpha'} \alpha^{-\frac{1}{2}} K(\rho') \cos \frac{1}{2} \phi d\alpha' \\ &= \frac{1}{\pi} \int_0^\infty e^{\alpha - \alpha' - \rho'(\alpha' \rho')^{-\frac{1}{2}}} \cos \frac{1}{2} \phi d\alpha'. \quad (3.41) \end{aligned}$$

By means of the substitution

$$\tan \frac{1}{2} \phi = \frac{\cosh u - \cos \theta}{\sin \theta},$$

this is reducible to the form

$$\tau_1 = \frac{e^\alpha \sin \theta}{\pi} \int_0^\infty \frac{e^{-\rho \cosh u} du}{\cosh u - \cos \theta}. \quad (3.42)$$

This integral has not been evaluated in finite terms, but, at the cost of considerable computation, values have been obtained sufficiently accurate to enable the isothermals to be plotted, and these are given in fig. 2, which also shows the temperature and heat transfer along

the axis. The corresponding isothermals for Boussinesq's "reduced" equation are shown, for comparison, in fig. 3.

Fig. 2.

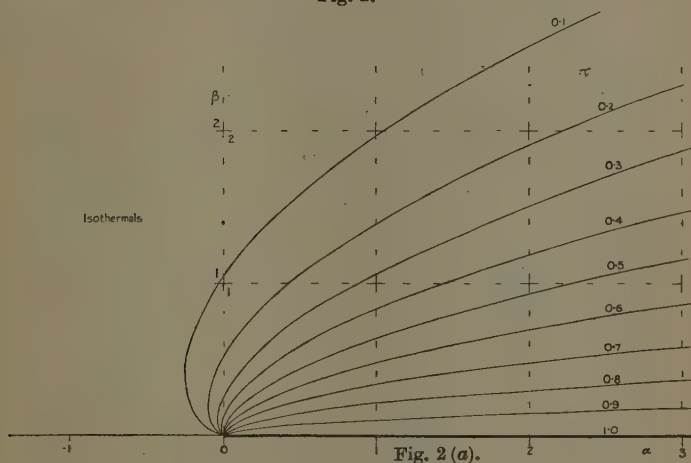


Fig. 2 (a).

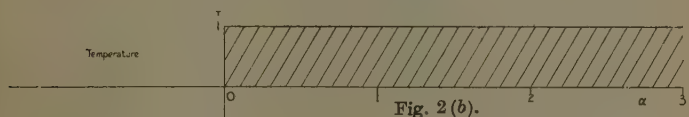


Fig. 2 (b).

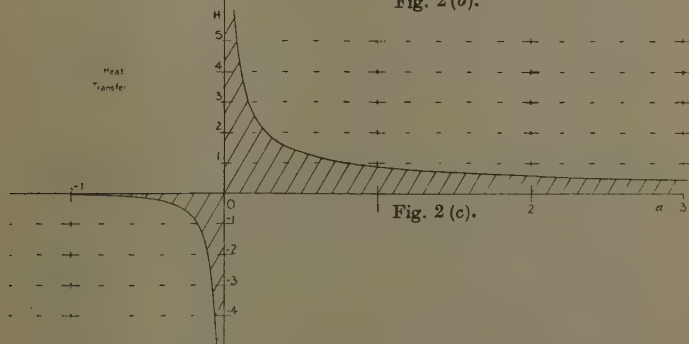


Fig. 2 (c).

In this figure it is to be noted that, since the "reduced" equation implies no heat propagation upstream, the whole region for which α is negative is one of zero temperature.

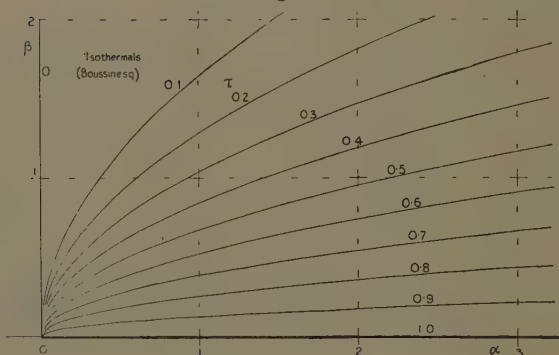
The calculation of τ_1 from the formula (3.42) started with the expansion of the denominator, giving

$$\begin{aligned}\tau_1 &= \frac{e^\alpha \sin \theta}{\pi} \sum_{n=0}^{\infty} \cos^n \theta \int_0^{\infty} \frac{e^{-\rho \cosh u} du}{\cosh^{n+1} u} \\ &= \frac{e^\alpha \sin \theta}{\pi} \sum_{n=0}^{\infty} \text{Ki}_{n+1}(\rho) \cos^n \theta, \quad \dots \quad (3.43)\end{aligned}$$

where

$$\text{Ki}_m(\rho) = \int_0^{\infty} \frac{e^{-\rho \cosh u} du}{\cosh^m u} \quad \dots \quad (3.5)$$

Fig. 3.



The more elementary properties of these functions, and a short table of their values, is given in the following paper.

Using these values of the Ki_m , τ_1 was calculated for the tabulated values of ρ and for every 10° of θ . For $\theta \leq 30^\circ$ and $\theta \geq 150^\circ$, the series (3.43) converges slowly, but the values were corrected by smoothing the differences of the sets for each value of ρ , the values for $\theta = 0$ and $\theta = 180^\circ$ being accurately known. For all this computation, and also for the method of correcting the values at the ends of the θ range, the author is greatly indebted to Mr. John Nayler, A.C.G.I., B.Sc.(Eng.).

The rate of heat loss per unit length of the α -axis (and per unit length perpendicular to the α - β plane) is $-k(\partial\tau_1/\partial\beta)_{\beta=0}$. Now, it is easily found that

$$\partial\tau_1/\partial\beta = -e^\alpha \{K_0(\rho) + K_1(\rho) \cos \theta\}/\pi, \quad \dots \quad (3.61)$$

and also that

$$\partial \tau_1 / \partial \alpha = e^\alpha K_1(\rho) \sin \theta / \pi. \quad (3.62)$$

Thus the rate of heat ions is

$$\begin{aligned} & ke^\alpha \{K_0(\alpha) + K_1(\alpha)\} / \pi \quad \alpha > 0 \\ \text{and} \quad & -ke^\alpha \{K_1(-\alpha) - K_0(-\alpha)\} / \pi \quad \alpha < 0 \end{aligned} \quad (3.63)$$

A graph of this is given in fig. 2(c). When $\alpha < 0$ the loss is negative—heat is transferred against the stream from the hot to the cold portion of the boundary. Of course, the discontinuity in temperature could not be practically maintained, and the solution is in this sense artificial. If the rise of temperature were spread over a small length of the α -axis—a practical possibility—the infinities in the heat loss would be removed, but except in the close neighbourhood of $\alpha = 0$, neither temperature distribution nor rate of heat loss would be considerably affected. The net heat loss from $-\infty$ up to $\alpha = \alpha_1$ is the principal value (in Cauchy's sense) of the integral of (3.63). This is found to be

$$(k/\pi) \{2\alpha_1 e^{\alpha_1} [K_0(\alpha_1) + K_1(\alpha_1)] - e^{\alpha_1} K_0(\alpha_1)\} \quad (3.74)$$

on one side of the α -axis. If α_1 is large, we may use the asymptotic expansion of the K functions, and if we use the first term only of these, this gives, as the heat loss from *both* sides, $8k\sqrt{(\alpha_1/2\pi)}$. If the case of a hot plate at temperature θ is considered, the loss H per unit width, from a length l measured from the leading edge is obtained by multiplying the above by θ , and substituting the value of α_1 , which is $cUl/2k$. We thus obtain

$$H/k\theta = 4\sqrt{(cUl/\pi k)}, \quad (3.7)$$

which is exactly the result obtained by Boussinesq, and also by Piercy and Winny, using different approximate methods. It is at first sight rather surprising that three different methods should lead to identically the same approximation; but closer examination shows that, although conditions near the leading edge will differ, the divergence will decrease fairly rapidly as we go downstream, and although the heat loss is great near (and indeed infinite at) the leading edge, the relative importance of this diminishes as the total length considered increases.

We return to our exact solution (3.42) since, despite—or rather on account of—the artificiality of the tempera-

ture distribution, it has very useful properties. It is, for the type of problem under discussion, analogous to the Heaviside "unit function" so much used in electrical transmission theory, and enables us to build up, at least formally, the solution for *any* prescribed temperature distribution along the α -axis. By reasoning exactly the same as that used in the electrical theory mentioned⁽⁸⁾, we deduce that, if the temperature along the α -axis is given by $g(\alpha)$, then the temperature at the point (α, β) is

$$\tau g(\alpha, \beta) = \int_{-\infty}^{\infty} \tau_1(\alpha - \alpha', \beta) g'(\alpha') d\alpha'. \quad (3.81)$$

It also follows from (3.81) and (3.61), that the rate of heat loss in the neighbourhood of $\alpha = \alpha_1$ is given by

$$q(\alpha_1) = k \left[\int_{-\infty}^{\alpha_1} e^{\alpha_1 - \alpha'} \{K_0(\alpha_1 - \alpha') - K_1(\alpha_1 - \alpha')\} g'(\alpha') d\alpha' \right. \\ \left. + \int_{\alpha_1}^{\infty} e^{\alpha_1 - \alpha'} \{K_0(\alpha' - \alpha_1) + K_2(\alpha' - \alpha_1)\} g'(\alpha') d\alpha' \right], \quad (3.82)$$

which is, of course, the solution of the integral equation

$$\pi k g(\alpha) = \int_{-\infty}^{\infty} e^{\alpha - \alpha'} K_0(|\alpha - \alpha'|) q(\alpha') d\alpha',$$

the form taken by (2.7) when $\beta = 0$ for our prescribed temperature distribution.

We refrain from entering into any more mathematical detail, but it seems worth while illustrating the isothermals and heat loss when the temperature is prescribed to be constant over a finite segment of the α -axis, and zero over the rest of it, since this is the case which Boussinesq used as the approximation from which he deduced the heat loss for a circular cylinder at constant temperature. Fig. 4 (a) shows the isothermals when the temperature is unity over a segment of length 2 units along the α -axis (the part thickened), and zero elsewhere along that axis; fig. 4 (c) shows the corresponding heat loss; fig. 5 exhibits the isothermals of Boussinesq's solution, in which the curious form near $\alpha = 2$ is a consequence of his "reduced" equation implying no conduction against the stream. According to Boussinesq's solution, the heat loss varies as $\alpha^{-\frac{1}{2}}$.

Fig. 4.

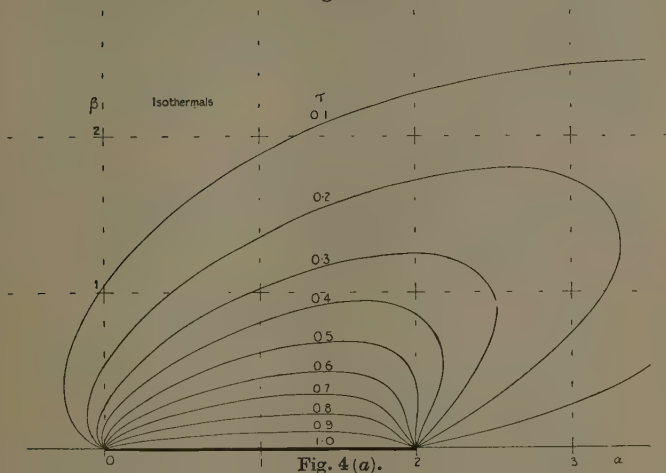


Fig. 4(a).

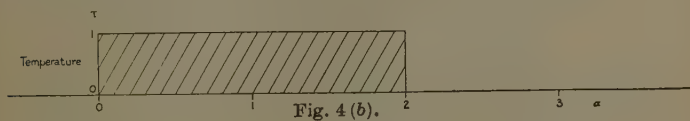


Fig. 4(b).

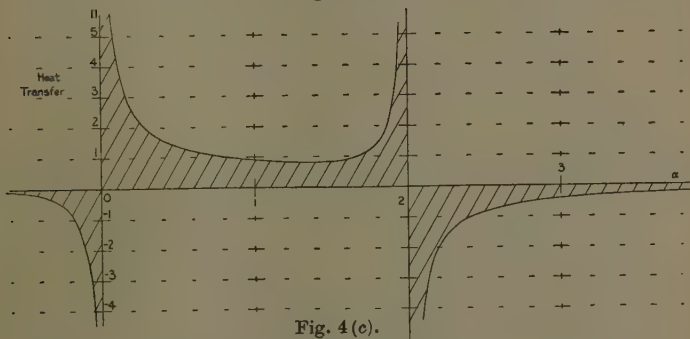


Fig. 4(c).

4. Uniform Distribution of Line-Sources along the Positive Half of the α -Axis.

The solution of this problem, which was taken by King* as the case which was sufficiently simple mathematically,

* *Loc. cit.*

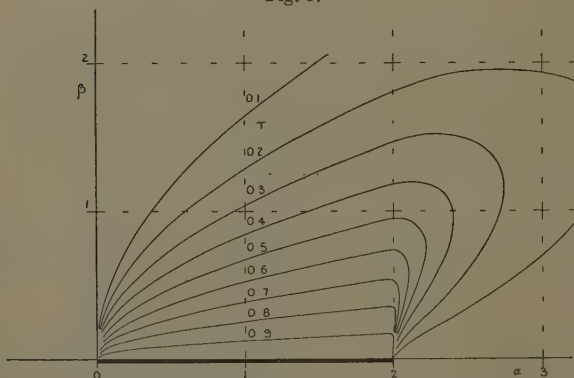
and, at the same time, a possibly sufficient approximation, to be used in calculating the heat loss from a circular cylinder, is implied in (2.7), for the special value $q(\alpha') = \text{const.}$ The constant can be taken as unity with no loss of generality.

We thus have

$$\pi k \tau_2 = \int_0^\infty e^{\alpha - \alpha'} K_0(\rho') d\alpha', \quad . \quad . \quad (4.1)$$

with the notation of fig. 1. This integral can be put into another form, cognate with the integral of the last para-

Fig. 5.



graph, and more convenient for computation, by use of the formula

$$K_0(\rho') = \frac{1}{2} \int_{-\infty}^{\infty} e^{-\beta \cosh v + i(\alpha - \alpha') \sinh v} dv,$$

whence we derive

$$2\pi k \tau_2 = \int_0^\infty e^{(\alpha - \alpha')} d\alpha' \int_{-\infty}^{\infty} e^{-\beta \cosh v + i(\alpha - \alpha') \sinh v} dv.$$

Changing the order of integration, as is evidently legitimate, we derive

$$\begin{aligned} 2\pi k \tau_2 &= e^\alpha \int_{-\infty}^{\infty} \frac{e^{-\beta \cosh v + i \alpha \sinh v} dv}{1 + i \sinh v} \\ &= e^\alpha \int_{-\infty}^{\infty} \frac{e^{-\rho \cosh(v + i\theta - i\pi/2)} dv}{1 + i \sinh v}. \end{aligned}$$

If we now write $v+i\theta-i\pi/2=u$, and note that if $0 \leq \theta \leq 2\pi$, the u -contour can be deformed into the real axis, we derive

$$\begin{aligned} 2\pi k\tau_2 &= e^\alpha \int_{-\infty}^{\infty} \frac{e^{-\rho \cosh u} (1 - \cosh u \cos \theta + i \sinh u \sin \theta) du}{(\cosh u - \cos \theta)^2} \\ &= 2e^\alpha \int_0^{\infty} \frac{e^{-\rho \cosh u} (1 - \cosh u \cos \theta) du}{(\cosh u - \cos \theta)^2} \\ &= 2e^\alpha \int_0^{\infty} e^{-\rho \cosh u} \frac{d}{du} \left(\frac{\sinh u}{(\cosh u - \cos \theta)} \right) du \\ &= 2e^\alpha \left\{ \left[\frac{e^{-\rho \cosh u} \sinh u}{(\cosh u - \cos \theta)} \right]_0^{\infty} \right. \\ &\quad \left. + \rho \int_0^{\infty} \frac{e^{-\rho \cosh u} \sinh^2 u du}{(\cosh u - \cos \theta)} \right\}. \end{aligned}$$

The integrated term vanishes at both limits, leaving

$$\pi k\tau_2 = \rho e^\alpha \int_0^{\infty} \frac{e^{-\rho \cosh u} \sinh^2 u du}{(\cosh u - \cos \theta)}. \quad (4.2)$$

If we expand the denominator and use the identity $\sinh^2 u = \cosh^2 u - 1$, we obtain

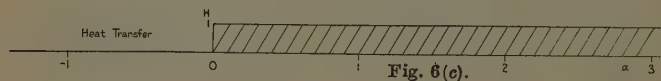
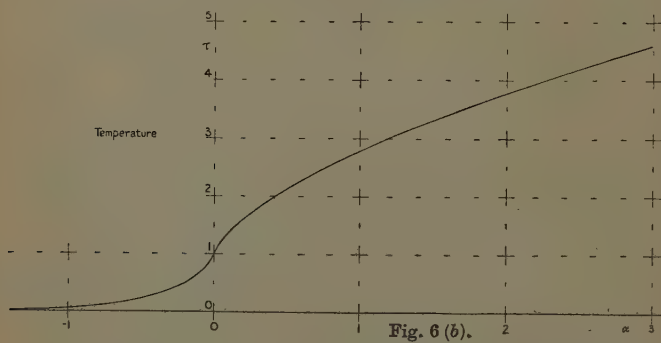
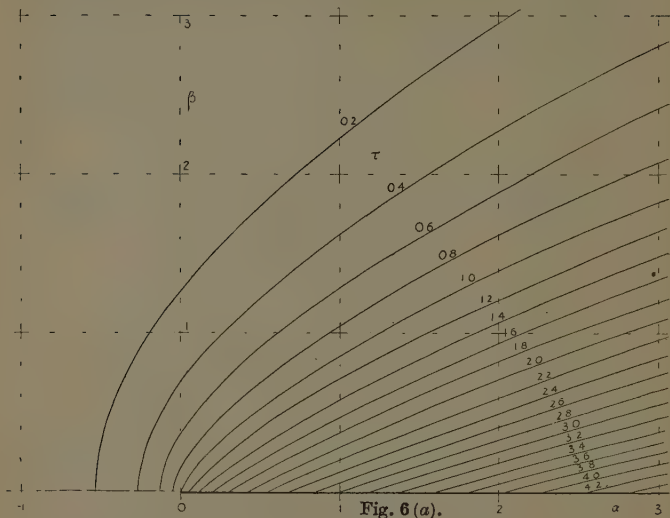
$$\pi k\tau_2 = \rho e^\alpha \sum_{n=0}^{n=\infty} \{ \text{Ki}_{n-1}(\rho) - \text{Ki}_{n+1}(\rho) \} \cos^n \theta. \quad (4.3)$$

The values of $\pi k\tau_2$ were calculated from this series, using the values of the Ki_n already mentioned and the same methods when $0 < \theta \leq 30^\circ$ and $150^\circ \leq \theta \leq 180^\circ$. The isothermals plotted from the results are shown in fig. 6 (a), the values attached to the curves being those of $\pi k\tau_2$. It is to be noted that, since there are no sources on the negative half of the α -axis, $\partial\tau_2/\partial\beta$ vanishes there, so that the solution is also valid when β is negative; we have thus obtained the temperature distribution due to uniform heat emission over a semi-infinite plate with a stream flowing parallel to it, and perpendicular to its edge-line.

We may also notice that

$$-k(\partial\tau_2/\partial\beta)_{\beta=0} = \begin{matrix} 0 & (\alpha < 0) \\ 1 & (\alpha > 0), \end{matrix}$$

Fig. 6.



so that $-k\partial\tau_2/\partial\beta$ and τ_1 satisfy the same boundary conditions, and the same differential equation; they must therefore be identical—an identity not difficult to verify.

The value of τ_2 along the α -axis can be expressed in finite terms (a fact that seemed to escape King, who carried out a considerable amount of computation, and whose results for $\int_0^x e^t K_0(t) dt$ are often several units in error in the fourth significant figure). By (4.2), when $\theta=0$,

$$\begin{aligned} (\pi k \tau_2)_{\theta=0} &= \alpha e^{\alpha} \int_0^{\infty} e^{-\alpha \cosh u} (1 + \cosh u) du \\ &= \alpha e^{\alpha} \{K_0(\alpha) + K_1(\alpha)\}, \quad . \quad . \quad . \quad (4.31) \end{aligned}$$

and the corresponding formula when $\theta=\pi$, so that α is negative, is

$$(-\alpha) e^{\alpha} \{K_1(-\alpha) - K_0(-\alpha)\}. \quad . \quad . \quad (4.32)$$

Along the β -axis ($\theta=\pi/2$), the temperature is given by

$$\begin{aligned} (\pi k \tau_2)_{\theta=\pi/2} &= \beta \{Ki_{-1}(\beta) - Ki_1(\beta)\} \\ &= \beta \{K_1(\beta) - Ki_1(\beta)\}. \quad . \quad . \quad . \quad (4.33) \end{aligned}$$

A graph of the temperature distribution along the axis is given in fig. 6 (b).

From the solution τ_2 , the solution for uniform emission over a strip of width γ (in the direction of flow) can be immediately written down. If the trace of the strip is the portion of the α -axis for which $0 < \alpha < \gamma$, we have

$$\tau_2' = \tau_2(\alpha, \beta) - \tau_2(\alpha - \gamma, \beta), \quad . \quad . \quad . \quad (4.4)$$

and isothermals for the case $\gamma=2$ are sketched in fig. 7 (a). The temperature variation along the α -axis is shown in fig. 7 (b). King, using essentially this solution in his attempt to approximate to the heat loss from a circular cylinder, took the temperature at the trailing edge of the plate as the temperature to be associated with the cylinder, so that, as pointed out by Piercy and Winny, there is a difference of temperature between the fluid and the temperature assumed for the cylinder, which changes sign as the obstacle is traversed.

We may also note that $\partial \tau_2' / \partial \beta = 0$ on the α -axis in the wake, so that this solution could be transformed to give a temperature and heat loss distribution for any cylindrical obstacle. As, however, neither temperature nor heat loss

per unit area would be constant over the surface of the cylinder, it seems hardly worth giving an example.

Fig. 7.

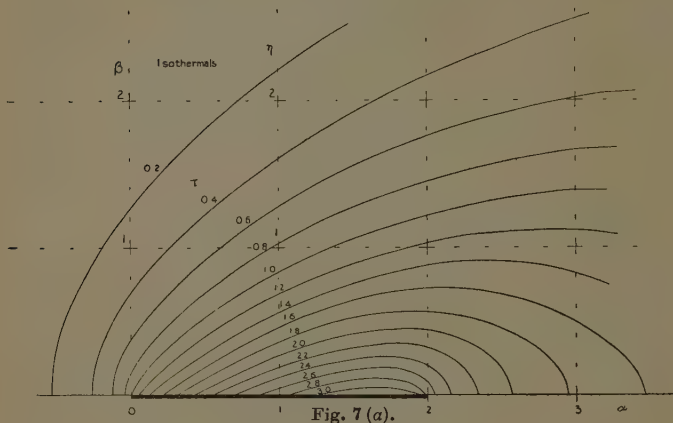


Fig. 7 (a).

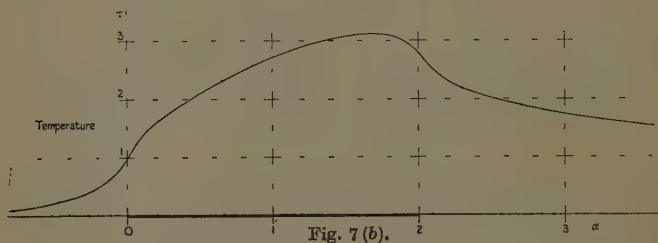


Fig. 7 (b).

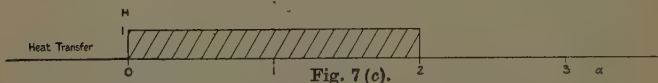


Fig. 7 (c).

5. Semi-Infinite Plane maintained at Constant Temperature.

The remarks at the end of the last section indicate that a solution making τ constant over one portion, and $\partial\tau/\partial\beta$ zero over the rest, of the α -axis is desirable. A solution has been found when the first of these is a portion of the axis extending to infinity in the down-stream

direction. Taking this portion to be the positive half of the axis, a transformation to parabolic coordinates (λ, μ) , given by

$$\alpha = \lambda^2 - \mu^2, \quad \beta = 2\lambda\mu \quad . \quad . \quad . \quad (5.1)$$

is indicated. In these coordinates the fundamental differential equation (2.4) becomes

$$\frac{\partial^2 \tau}{\partial \lambda^2} + \frac{\partial^2 \tau}{\partial \mu^2} = 4 \left(\lambda \frac{\partial \tau}{\partial \lambda} - \mu \frac{\partial \tau}{\partial \mu} \right). \quad . \quad . \quad . \quad (5.2)$$

Happily the general solution of this equation is not here necessary, since a solution which is a function of μ only, which does not vanish when $\mu=0$, and which tends to zero as $\mu \rightarrow \infty$, satisfies all the conditions—and such a solution exists. The differential equation for such a solution is

$$\frac{d^2 \tau}{d\mu^2} = -4\mu \frac{d\tau}{d\mu}. \quad . \quad . \quad . \quad (5.31)$$

The complete solution of this is readily found to be

$$\tau = C \int^\mu e^{-2t^2} dt + D, \quad . \quad . \quad . \quad (5.32)$$

C and D being any constants. It is evident that if τ is to vanish when $\mu = \infty$, one limit must be ∞ , so that we have

$$\tau = C \int_\mu^\infty e^{-2t^2} dt. \quad . \quad . \quad . \quad (5.33)$$

If we choose C so that the temperature is unity when $\mu=0$, we find that

$$\tau_3 = \frac{2\sqrt{2}}{\sqrt{\pi}} \int_\mu^\infty e^{-2t^2} dt = \sqrt{\frac{2}{\pi}} \text{Hh}_0(\tfrac{1}{2}\mu) \quad . \quad (4.34)$$

is the required solution, the notation being that of the British Association Mathematical Tables, vol. 1. The isothermals are thus parabolas with their focus at the edge of the plane, and they are readily plotted with the help of the tables mentioned, or indeed of any table of the probability integral. Their spacing is shown in fig. 8(a).

The rate of heat loss per unit area, on *one* side of the plane, is

$$\begin{aligned} (-k \partial \tau_3 / \partial \beta)_{\beta=0} &= \left\{ -k \frac{\lambda}{2(\lambda^2 + \mu^2)} \frac{\partial \tau}{\partial \mu} \right\}_{\mu=0} \\ &= \frac{k}{\lambda} \sqrt{\frac{2}{\pi}} = k \sqrt{(2/\pi \alpha)}. \quad . \quad . \quad (5.41) \end{aligned}$$

Fig. 8.

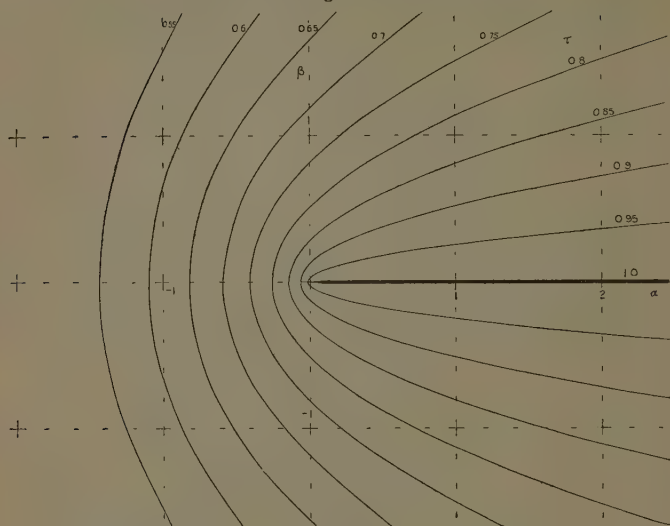


Fig. 8 (a).

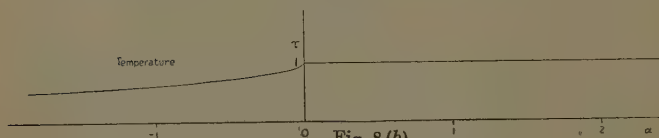


Fig. 8 (b).

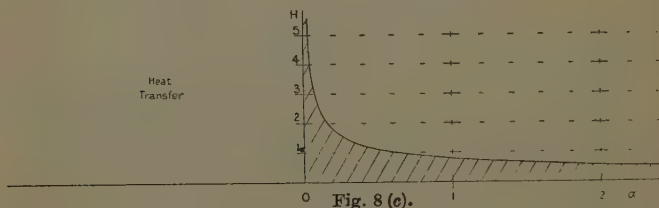


Fig. 8 (c).

The total loss over a length $l (= 2k\alpha/cU)$ is

$$\begin{aligned} H &= 2k\sqrt{2/\pi} \int_0^\alpha \alpha^{-\frac{1}{2}} d\alpha \\ &= 4k\sqrt{2\alpha/\pi} = 4k\sqrt{cUl/\pi k}. \quad (5.42) \end{aligned}$$

If the temperature of the plane is θ instead of unity, we deduce that

$$H/k\theta = 4\sqrt{(cUl/\pi k)}. \quad (5.43)$$

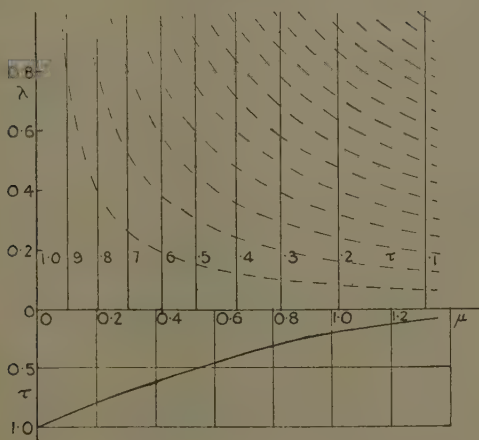
which is seen to agree exactly with (3.8).

Inserting the result (5.41) in the integral equation (2.7), we find that

$$\int_{\mu}^{\infty} e^{-2t^2} dt = \frac{e^{\alpha}}{2\pi} \int_0^{\infty} \frac{e^{-\alpha'} K_0(\rho)}{\sqrt{\alpha'}} d\alpha',$$

an identity not difficult to verify.

Fig. 9.



One rather interesting example of the transformation of the above solution presents itself. If λ and μ are taken as rectangular coordinates, the fluid flow is that of a stream impinging normally on a plane wall, the stream-lines being, of course, rectangular hyperbolæ. It then appears that the isotherms are parallel to the wall, spaced as in fig. 9, in which the full lines are the isotherms, the dotted ones the stream-lines, and the graph below shows the way in which temperature falls off as we recede from the wall. In this case, too, the rate of heat loss is constant over the wall.

6. *Concluding Remarks.*

The merit of the three main solutions given above is that they are mathematically accurate deductions from the physical and boundary conditions assumed. In addition to the idealisation of the assumptions upon which they rest, they suffer from the disadvantage that the "solid" is semi-infinite, while the first also has the disadvantage that the heat-transfer is not confined to a portion of the α -axis, so that the whole axis is part of the "solid" boundary, across which the solution cannot be continued. At the same time, the heat loss for a moderately long solid, calculated from either the first or the third solution, agrees approximately with the result of Boussinesq, which confirms the legitimacy of the assumption used by him in forming the "reduced" equation.

The accurate solution of the problem for an obstacle of finite cross-section, maintained at a constant temperature, is still to be found. The use of elliptic coordinates is indicated, and the solutions will necessarily involve Mathieu functions. The functions of trigonometric type have been studied and tabulated⁽⁹⁾, but the associated functions of hyperbolic type, and in particular those vanishing at infinity, do not seem to have received much attention. The author has made some progress in this direction, and hopes that the investigation along these lines may ultimately be completed, but a very great amount of numerical work will be required before arithmetical results can be given.

Further points of mathematical interest are the solution of (5.1) in the form $L(\lambda)M(\mu)$, where L and M will be associated parabolic cylinder functions and the expansion of an arbitrary function in terms of the L functions.

The corresponding three-dimensional problem does not seem open to the same line of treatment, for even when a stream-function exists, as for flow symmetrical about an axis, it differs in dimensions from the velocity potential; there would seem to be no possibility of reducing all cases to a differential equation independent of the shape of the hot solid.

References.

- (1) Boussinesq, *Comptes Rendus*, cxxxiii. p. 257 (1901); 'Théorie Analytique de la Chaleur,' t. ii. (1903); *J. de Math.* (6) i. (1901).
- (2) Russell, *Phil. Mag.* xx. p. 591 (1910).

- (3) Wilson, Proc. Camb. Phil. Soc. xii. p. 406 (1904).
 (4) King, Phil. Trans. Roy. Soc. A, 214, p. 373 (1914).
 (5) Piercy and Winny, Phil. Mag. (7) xvi. p. 391 (1933).
 (6) Zeilon, Appendix to Oseen's 'Hydrodynamik,' Leipsig (1927).
 (7) Southwell and Squire, Phil. Trans. Roy. Soc. A, cccxxii. p. 27 (1933).
 (8) See, for example, Carson, 'Electric Circuit Theory and Operational Calculus,' New York (1926).
 (9) Ince, Proc. Roy. Soc. Edin. lii. p. 356 (1932).

Since the above was completed, two papers by Small (Phil. Mag. (7) xix. p. 21 and p. 251 (1935)) have appeared. The first of these contains a novel derivation of Boussinesq's results for the reduced equation, and a numerical second approximation, while the second gives some experimental results for the circular cylinder.

XXV. *A Short Table of the Functions $Ki_n(x)$, from $n=1$ to $n=16$. By W. G. BICKLEY, D.Sc., and JOHN NAYLER, A.C.G.I., B.Sc.(Eng.), D.I.C.**

THE functions Ki_n have been calculated in order to obtain numerical results in the solution of certain problems in heat convection, treated in the preceding paper. The computations were carried out rather more elaborately than was absolutely necessary for that purpose, and the results are put on record so that they may be available if, as is not unlikely, other investigations necessitate the use of these functions.

The fundamental definition is

$$Ki_n(x) = \int_0^\infty \frac{e^{-x \cosh u} du}{\cosh^n u} \quad \dots \quad (1)$$

Evidently,

$$Ki_0(x) = K_0(x), \quad \dots \quad (2)$$

$K_0(x)$ being the Bessel function of the second kind, with "imaginary argument," as defined by Watson. It is also easy to verify that

$$Ki_n(x) = \int_x^\infty Ki_{n-1}(t) dt, \quad \dots \quad (3)$$

and

$$Ki_{n-1}(x) = -Ki'_n(x), \quad \dots \quad (4)$$

so that the functions are obtained from $K_0(x)$ by successive integrations; hence the notation employed.

* Communicated by the Authors.

	Ki ₁ .	Ki ₂ .	Ki ₃ .	Ki ₄ .
0.0 ..	1.570 796 327	1.000 000 000	0.785 398 163	0.666 666 667
0.05 ..	1.365 166 831	.927 225 375	.737 258 632	.628 615 386
0.1 ..	1.228 631 883	.862 521 290	.692 543 328	.592 883 812
0.15 ..	1.117 896 549	.803 940 334	.650 904 829	.559 309 809
0.2 ..	1.023 679 878	.750 458 533	.612 064 471	.527 746 716
0.3 ..	.868 832 269	.656 147 929	.541 862 954	.470 128 884
0.4 ..	.745 203 394	.575 660 412	.480 375 441	.419 084 002
0.5 ..	.643 693 806	.506 373 657	.426 358 256	.373 805 030
0.6 ..	.558 890 473	.446 366 680	.378 791 860	.333 597 509
0.7 ..	.487 198 347	.394 159 632	.336 825 253	.297 860 143
0.8 ..	.426 061 805	.348 575 863	.299 739 399	.266 069 884
0.9 ..	.373 578 804	.308 659 297	.266 921 357	.237 770 099
1.0 ..	.328 286 478	.273 620 752	.237 845 082	.212 560 967
1.1 ..	.289 031 851	.242 800 994	.212 056 694	.190 091 553
1.2 ..	.254 888 907	.215 644 180	.189 162 878	.170 053 199
1.3 ..	.225 102 780	.191 678 130	.168 821 575	.152 173 942
1.4 ..	.199 050 709	.170 499 270	.150 734 408	.136 213 787
1.5 ..	.176 213 863	.151 760 906	.134 640 424	.121 960 657
1.6 ..	.156 156 459	.135 163 924	.120 310 892	.109 226 918
1.7 ..	.138 509 952	.120 449 312	.107 544 931	.097 846 386
1.8 ..	.122 960 838	.107 392 071	.096 165 816	.087 671 727
1.9 ..	.109 241 097	.095 796 207	.086 017 832	.078 572 206
2.0 ..	.097 120 592	.085 490 579	.076 963 590	.070 431 721
3.0 ..	.030 848 237	.027 924 583	.025 646 500	.023 818 125

	Ki ₅ .	Ki ₆ .	Ki ₇ .	Ki ₈ .
0.0 ..	0.589 048 623	0.533 333 333	0.490 873 852	0.457 142 857
0.05 ..	.556 676 599	.504 698 130	.464 929 809	.433 253 731
0.1 ..	.526 148 433	.477 634 947	.440 377 842	.410 626 678
0.15 ..	.497 352 266	.452 054 424	.417 141 607	.389 194 020
0.2 ..	.470 183 944	.427 872 594	.395 149 091	.368 891 790
0.3 ..	.420 348 644	.383 393 966	.354 627 283	.331 440 029
0.4 ..	.375 939 222	.343 622 099	.318 313 479	.297 826 127
0.5 ..	.336 339 771	.308 045 872	.285 763 072	.267 651 940
0.6 ..	.301 009 271	.276 211 918	.256 579 618	.240 531 329
0.7 ..	.269 471 350	.247 717 661	.230 409 415	.216 236 617
0.8 ..	.241 305 745	.222 205 292	.206 936 733	.194 389 566
0.9 ..	.216 141 087	.199 356 528	.185 879 608	.174 767 785
1.0 ..	.193 648 758	.178 888 038	.166 986 120	.157 141 552
1.1 ..	.173 537 617	.160 547 440	.150 031 102	.141 305 972
1.2 ..	.155 549 453	.144 109 781	.134 813 227	.127 077 451
1.3 ..	.139 455 043	.129 374 452	.121 152 425	.114 291 445
1.4 ..	.125 050 725	.116 162 461	.108 887 580	.102 800 453
1.5 ..	.112 155 411	.104 314 029	.097 874 500	.092 472 221
1.6 ..	.100 607 971	.093 686 469	.087 984 096	.083 188 145
1.7 ..	.090 264 942	.084 152 305	.079 100 774	.074 841 845
1.8 ..	.080 998 516	.075 597 610	.071 120 999	.067 337 884
1.9 ..	.072 694 775	.067 920 526	.063 952 011	.060 590 630
2.0 ..	.065 252 122	.061 029 964	.057 510 687	.054 523 236
3.0 ..	.022 314 719	.021 053 569	.019 977 877	.019 047 420

	Ki_9 .	Ki_{10} .	Ki_{11} .	Ki_{12} .
0.0 ..	0.429 514 621	0.406 349 206	0.386 563 159	0.369 408 369
0.05 ..	.407 260 111	.385 434 815	.366 773 194	.350 579 318
0.1 ..	.386 168 215	.365 603 820	.348 001 622	.332 714 078
0.15 ..	.366 177 538	.346 799 641	.330 195 700	.315 763 063
0.2 ..	.347 229 975	.328 968 683	.313 305 439	.299 679 249
0.3 ..	.312 247 145	.296 026 031	.282 084 850	.269 937 181
0.4 ..	.280 814 092	.266 400 975	.253 989 689	.243 158 137
0.5 ..	.252 567 309	.239 757 045	.228 705 323	.219 045 586
0.6 ..	.227 180 960	.215 792 203	.205 949 012	.197 332 836
0.7 ..	.204 362 917	.194 235 276	.185 466 649	.177 780 014
0.8 ..	.183 851 214	.174 842 771	.167 029 836	.160 171 347
0.9 ..	.165 410 891	.157 396 014	.150 433 261	.144 312 728
1.0 ..	.148 831 165	.141 698 597	.135 492 344	.130 029 527
1.1 ..	.133 922 916	.127 574 087	.122 041 131	.117 164 621
1.2 ..	.120 516 424	.114 863 975	.109 930 398	.105 576 634
1.3 ..	.108 459 361	.103 425 838	.099 025 953	.095 138 347
1.4 ..	.097 614 984	.093 131 695	.089 207 112	.085 735 270
1.5 ..	.087 860 526	.083 866 525	.080 365 387	.077 264 368
1.6 ..	.079 085 749	.075 526 946	.072 402 966	.069 632 902
1.7 ..	.071 191 650	.068 020 030	.065 232 194	.062 757 398
1.8 ..	.064 089 312	.061 262 234	.058 773 998	.056 562 719
1.9 ..	.057 698 860	.055 178 447	.052 957 287	.050 981 224
2.0 ..	.051 948 533	.049 701 133	.047 718 100	.045 952 018
3.0 ..	.018 232 948	.017 512 683	.016 870 075	.016 292 314

	Ki_{13} .	Ki_{14} .	Ki_{15} .	Ki_{16} .
0.0 ..	0.354 349 562	0.340 992 341	0.329 038 879	0.318 259 518
0.05 ..	.336 353 993	.323 728 675	.312 424 603	.302 226 528
0.1 ..	.319 275 568	.307 341 657	.296 651 402	.287 003 041
0.15 ..	.303 067 349	.291 786 616	.281 676 572	.272 548 083
0.2 ..	.287 684 810	.277 021 162	.267 459 582	.258 822 755
0.3 ..	.259 230 001	.249 700 202	.241 147 222	.233 415 178
0.4 ..	.233 598 643	.225 081 082	.217 429 513	.210 506 853
0.5 ..	.210 509 523	.202 895 764	.196 049 908	.189 851 367
0.6 ..	.189 709 562	.182 902 900	.176 777 305	.171 226 664
0.7 ..	.170 970 985	.164 885 164	.159 403 515	.154 432 635
0.8 ..	.154 088 778	.148 646 847	.143 740 985	.139 288 940
0.9 ..	.138 878 403	.134 011 701	.129 620 726	.125 633 048
1.0 ..	.125 173 738	.120 820 994	.116 890 509	.113 318 477
1.1 ..	.112 825 238	.108 931 764	.105 413 160	.102 213 199
1.2 ..	.101 698 266	.098 215 244	.095 065 180	.092 198 216
1.3 ..	.091 671 602	.088 555 447	.085 734 900	.083 166 265
1.4 ..	.082 636 102	.079 847 897	.077 322 261	.075 020 662
1.5 ..	.074 493 487	.071 998 475	.069 736 727	.067 674 253
1.6 ..	.067 155 258	.064 922 396	.062 896 697	.061 048 472
1.7 ..	.060 541 717	.058 543 276	.056 729 024	.055 072 496
1.8 ..	.054 581 092	.052 792 297	.051 167 211	.049 682 476
1.9 ..	.049 208 741	.047 607 456	.046 151 700	.044 820 850
2.0 ..	.044 366 445	.042 932 886	.041 628 717	.040 435 724
3.0 ..	.015 769 327	.015 293 077	.014 857 069	.014 455 991

There is a recurrence formula connecting four consecutive functions, obtained as follows:

$$\begin{aligned}
 Ki_{n-2}(x) - Ki_n(x) &= \int_0^\infty \frac{e^{-x \cosh u} \sinh^2 u \, du}{\cosh^n u} \\
 &= \left[-\frac{e^{-x \cosh u} \sin u}{x \cosh^n u} \right]_0^\infty \\
 &\quad + \frac{1}{x} \int_0^\infty \frac{e^{-x \cosh u} (\cosh^2 u - n \sinh^2 u) \, du}{\cosh^{n+1} u} \\
 &= \frac{1}{x} \int_0^\infty e^{-x \cosh u} \left\{ \frac{n}{\cosh^{n+1} u} - \frac{n-1}{\cosh^{n-1} u} \right\} du \\
 &= \{n Ki_{n+1}(x) - (n-1) Ki_{n-1}(x)\} / x,
 \end{aligned}$$

or,

$$n Ki_{n+1}(x) = (n-1) Ki_{n-1}(x) + x \{ Ki_{n-2}(x) - Ki_n(x) \}. \quad (5)$$

Values of Ki_1 and Ki_2 were computed for each value of the argument from the series obtained by successive integration of the series for $K_0(x)$, the constants of integration being the values of $Ki_1(0)$ and $Ki_2(0)$, *i. e.*, $\pi/2$ and 1 respectively. Eleven decimal places were retained, and the values were checked by the recurrence formula (5), using $n=0$ and $n=1$, ($Ki_{-1}(x) = K_1(x)$). The recurrence formula, which converges, in the sense that errors gradually diminish, was now used to calculate successively $Ki_3, Ki_4, \dots, Ki_{16}$. The values at interval 0.1 of x were differenced, and the differences showed that no error of more than 1 or 2 was present in the eleventh place. The values at $x=0.05, 0.15$, and 3.0 were checked by Taylor's series for $n > 5$ (which automatically checks the values for $n \leq 5$). Taylor's series is here very convenient, since by (3) the successive derivatives required are the values of the functions of lower order. Indeed, owing to this fact, Taylor's series is probably the most convenient interpolation formula to apply, should values for intermediate arguments be required.

For large arguments, when required, there is, of course, an asymptotic expansion. This can be obtained by

successive integration of that for $K_0(x)$ —a process known to be legitimate—and the result is

$$K_{i_n}(x) \sim e^{-x} \sqrt{\left(\frac{\pi}{2x}\right)} \cdot \left\{ 1 - \frac{4n+1}{8x} + \frac{3(16n^2+24n+3)}{2!(8x)^2} - \frac{3 \cdot 5 \cdot (64n^3+240n^2+212n+15)}{3!(8x)^3} \dots \right\}. \quad (6)$$

The law of the coefficients is not evident, but if

$$K_{i_n}(x) \sim e^{-x} \sqrt{\left(\frac{\pi}{2x}\right)} \cdot \left\{ A_n + \frac{B_n}{x} + \frac{C_n}{x^2} + \frac{D_n}{x^3} + \dots \right\},$$

we find

$$A_{n+1} = A_n,$$

$$B_{n+1} = B_n - A_{n+1}/2,$$

$$C_{n+1} = C_n - 3B_{n+1}/2,$$

$$D_{n+1} = D_n - 5C_{n+1}/2, \dots,$$

and starting with $A_0=1$, $B_0=-1/8$, $C_0=1^2 \cdot 3^2/2!8^2$, $D_0=-1^2 \cdot 3^2/3!8^3$, etc., the coefficients can be successively calculated.

XXVI. *The Absorption Band Spectrum of Selenium.*
By THOMAS E. NEVIN, *University College, Dublin* *.

Introduction.

THE bands which constitute the main absorption spectrum of selenium are degraded to the red, and lie in the region $\lambda\lambda$ 3239–4600. They have been investigated by Diestelmeier ⁽¹⁾, Evans and Antonoff ⁽²⁾, Fox and Dobbie ⁽³⁾, Rosen ⁽⁴⁾, and Moraczewska ⁽⁵⁾. The most complete investigation is that of Rosen, who gave a vibrational analysis of the bands and showed that the wave-lengths agreed with those of heads in the emission spectrum and the fluorescence spectrum excited by white light. Two new systems lying in the regions $\lambda\lambda$ 2099–2895 and $\lambda\lambda$ 2758–3150 were discovered by Moraczewska, in addition to a number of new bands belonging to the system analyzed by Rosen. Olsson ⁽⁶⁾ has made a rota-

* Communicated by Prof. J. J. Nolan, M.A., D.Sc.

tional analysis of five emission bands which also appear in absorption in Rosen's system and found they are due to a $^1\Sigma \rightarrow ^1\Sigma$ transition. In addition, from measurements of bands due to the molecule $\text{Se}_{80}\text{Se}_{80}$, he has shown that Rosen's values of ν' must be increased by five units.

The present paper deals only with the system described by Rosen. The dispersion he used was very small (300 cm^{-1} per mm.) and the values of $\Delta G(\nu + \frac{1}{2})$, which should be the same for any row or column of the table of ν' and ν'' progressions show large discrepancies, and many of the bands for low values of ν'' are very diffuse. It was thought that these points were worth further investigation.

Experimental.

The absorption cell was of fused quartz 15 cm. long and 3 cm. diameter, with flat ends of transparent fused quartz. After baking out, .01 gm. of pure selenium was introduced and the cell re-exhausted with an oil diffusion pump, backed by a Hyvac pump, and sealed off. It was inserted in an iron tube, which could be heated electrically to about 900° . As sources of continuous spectrum a water-cooled hydrogen tube of the Bay and Steiner⁽⁷⁾ pattern, taking 1 amp. at 3000 volts, was used up to λ 3650, and a tungsten filament lamp above this point. Photographs of the absorption spectrum were taken at different temperatures in the second order of a two-metre grating in a stigmatic mounting, with a dispersion of 8.8 Å./mm., and in the first order of a 21-foot grating in an Eagle mounting, with a dispersion of 2.6 Å./mm. An iron comparison spectrum was used. On the large grating plates the heads above λ 3500 were obscured by the overlapping rotational structure of other bands. The wavelengths of the stronger heads below this point are probably correct to about .03 Å. The heads above λ 3500 have been measured only on the small grating plates.

Vibrational Analysis.

Below λ 3570 each strong band has four heads, two strong heads with a weaker head on either side, of which that on the short-wave side is the more intense. When photographed in the first order of the small grating, which

has a dispersion of 18 Å./mm., the heads are blended together so that the bands appear very diffuse, in agreement with Rosen's observation.

The less refrangible of the two strong heads is due to the molecule $\text{Se}_{80}\text{Se}_{80}$. The other three are due to an isotope effect which will be discussed in the next section. The wave-lengths, wave-numbers, intensities, and vibrational quantum numbers are given in the first four columns of Table I. The intensity estimates are not of much significance, except over a short range of wave-lengths. Only a range of about 200 Å. could be measured on a single plate, and comparisons of intensities between different plates, necessarily taken at different temperatures, are inevitably very rough. The bands for which an isotope effect has been observed are marked with an asterisk. The other bands are, therefore, a blend of the four isotope heads. Between $\lambda 3570$ and $\lambda 3700$, where the calculated isotope effect amounts to several wave-numbers, the heads are somewhat diffuse and difficult to measure. Above $\lambda 3700$ they are quite sharp.

Rosen's analysis has been found essentially correct. The best agreement between the observed and calculated positions of the isotope heads is obtained, in agreement with Olsson, if Rosen's values of v' are increased by five units. The wave-numbers of the heads can be represented by the formula

$$\begin{aligned} \nu = & 26083.5 + 265.1(v' + \tfrac{1}{2}) - 1.878(v' + \tfrac{1}{2})^2 \\ & - [381.6(v'' + \tfrac{1}{2}) - 1.44(v'' + \tfrac{1}{2})^2 + .0088(v'' + \tfrac{1}{2})^3]. \end{aligned}$$

The difference between the observed wave-numbers and the values calculated from this formula (O—C) are given in column 5 of Table I. For all except the bands belonging to the initial levels $v'=7-11$, 20-22 the agreement is within the limits of the error of measurement. The values of O—C are given in Table II. For the levels 8-22 the values are calculated from the wave-numbers of the heads for which an isotope effect has been observed. For the levels 5-7, for which no isotope effect has been found, they are the mean of the values for all bands belonging to a particular level. The discrepancies in the case of the levels $v'=7-11$ are apparently due to the existence of large perturbations. Perturbations of band-heads ⁽⁸⁾ have been found in the case of the Ångström

TABLE I.
Heads due to $\text{Se}_{80}\text{Se}_{80}$.

1.	2.	3.	4.	5.	1.	2.	3.	4.	5.
v', v'' .	λ (in air).	Int.	ν (in vac.).	O—C.	v', v'' .	λ (in air).	Int.	ν (in vac.).	O—C.
22, 0	3239	0	30865	—32	9, 3	3686·3	3	27120	+22
21, 0	3255·50*	5	708·4	—16·0	10, 4	3707·7	4	26963	+18
20, 0	3274·03*	8	534·6	—3·5	8, 3	3718·2	2	887	+20
19, 0	3293·94*	9	350·0	+1·8	6, 2	3733·3	2	777	+3
18, 0	3315·32*	9	154·3	—0·1	9, 4	3739·5	4	734	+17
17, 0	3337·14*	9	29957·2	+0·2	10, 5	3760·5	4	584	+20
16, 0	3359·71*	9	755·9	+0·3	8, 4	3771·9	2	504	+18
15, 0	3383·17*	9	549·6	—1·1	9, 5	3794·2	4	349	+12·5
14, 0	3407·13*	9	341·8	—0·1	7, 4	3806·2	2	266	+14
13, 0	3432·02*	9	129·0	—0·3	10, 6	3815·4	4	202	+19
14, 1	3451·5	2	28965	+4·5	8, 5	3828·4	2	113	+8
12, 0	3457·26*	9	916·4	+3·2	6, 4	3843·0	2	014	+2
13, 1	3477·46*	6	748·4	+0·4	9, 6	3849·9	3	25967	+11
11, 0	3483·51*	9	698·5	+5·4	7, 5	3863·1	2	879	+9
14, 2	3497·95*	6	580·0	+0·9	10, 7	3871·2	3	824	+22
10, 0	3508·5	6	494	+25	5, 4	3879·7	2	768	—2
13, 2	3524·28*	5	366·5	—0·4	8, 6	3885·0	4	733	+9
11, 1	3530·43*	7	317·1	+5·4	6, 5	3900·4	2	631	—5
9, 0	3537·87*	5	258·5	+16·8	9, 7	3906·9	4	589	+24
14, 3	3545·41*	7	197·5	—0·9	7, 6	3920·3	4	501	+12
12, 2	3551·1	1	152	+1	10, 8	3930·3	1	436	+15
10, 1	3556·80*	6	107·2	+19·3	5, 5	3938·5	2	383	—6
8, 0	3566·48*	6	030·9	+20·5	8, 7	3942·9	4	355	+11
13, 3	3572·13	2	27986·5	+0·6	6, 6	3959·3	3	250	—1
9, 1	3585·1†	6	885	+25	9, 8	3965·8	3	209	+15
7, 0	3597·2	3	791	+16	7, 7	3980·1	3	118	+9·5
12, 3	3601·2	6	761	—9	10, 9	3991·1	2	049	+9
10, 2	3605·51*	6	727·4	+20·6	5, 6	3998·6	1	002	—6
8, 1	3615·1†	6	654	+25	8, 8	4002·7	1	24976	+13
13, 4	3621·0	5	609	+4	6, 7	4019·9	1	869	—1
11, 3	3628·1	4	555	+5	9, 9	4024·6	1	840	+27
9, 2	3635·3	4	500	+21	7, 8	4041·0	1	739	+12
7, 1	3645·9	5	420	+26	10, 10	4052·2	1	671	+12
10, 3	3656·2	5	343	+17	8, 9	4064·0	1	600	+18
8, 2	3665·7	4	272	+24	6, 8	4082·3	1	489	+0
6, 1	3681·3	1	157	+2	7, 9	4102·6	1	368	+22

* Bands for which an isotope effect has been observed.

† Diffuse.

CO bands ($v''=1$), the CO Cameron bands ($v'=1$), CS ($v'=1$), and in many levels of S_2 . In these cases it has been shown that the perturbations arise from the displacement of a number of lines near the heads of the bands, so that the heads themselves appear perturbed. The initial levels of the bands analyzed by Olsson, (10, 4), (10, 5), (10, 6), (8, 6), and (9, 7), are perturbed, but his analysis does not disclose the existence of any rotational perturbations. Unless we assume the existence of vibrational perturbations, the observed displacements must arise from rotational perturbations of the initial levels in which all the levels are displaced regularly.

The discrepancies between the observed and calculated values in the case of the levels $v'=20-22$ are probably

TABLE II.
Values of O—C for the Initial Levels.

v'	O—C.	v'	O—C.	v'	O—C.
5	— 4.7	11	+5.4	17	+ 0.2
6	+ 0.8	12	+3.2	18	— 0.1
7	+18.3	13	+0.1	19	+ 1.8
8	+20.5	14	0.0	20	— 3.5
9	+16.8	15	—1.1	21	—16.0
10	+19.9	16	+0.3	22	—32

due to a change in the law of force between the nuclei at $v'=20$. The values of $\Delta G(v'+\frac{1}{2})$ for $v'=18, 19, 20$, and 21 are 195.7, 184.6, 173.8, and 157 respectively, and the second differences are 11.1, 10.8, and 17. A linear extrapolation gives for the heat of dissociation 5900 cm^{-1} . The change in the law of force occurs 4509 cm^{-1} above the lowest level, at which point the molecule has 73 per cent. of the energy required for dissociation. This result is in agreement with similar observations ⁽⁹⁾ in the spectra of O_2 , Cl_2 , Br_2 , I_2 , etc.

The heat of dissociation for the lower state has not been calculated. The formula (1) for this state cannot be correct for large values of v'' , as the calculated values of $\Delta G(v''+\frac{1}{2})$ begin to increase above $v''=6$, though it represents the results fairly well over the range of the observations.

A number of bands have been measured which do not appear to belong to this system and are given in Table III. Some of these have been measured by Rosen and assigned to the $v' = 11$ progression, but the difference between the observed and calculated values is far outside the possible errors of measurement.

TABLE III.
List of Unclassified Bands.

λ (in air).	Int.	λ (in air).	Int.	λ (in air).	Int.
3608.4	5	3782.0	2	4074.4	1
3674.8	4	3838.5	1	4093.1	1
3695.8	3	3953.5	3		
3728.0	2	4013.8	1		

Isotope Effect.

The isotopes of selenium and their relative abundance, according to Aston ⁽¹⁰⁾ are as follows:—

Mass number	74	76	77	78	80	82
Relative abundance .	.9	9.5	8.3	24	48	9.3

The more refrangible of the pair of strong heads observed below $\lambda 3570$ falls in the position calculated for the molecule $\text{Se}_{78}\text{Se}_{80}$. On account of the large values of v' , which occur for small values of v'' , one must, in calculating the separation of the heads, use the formula given by Patkowski and Curtis ⁽¹¹⁾:

$$\Delta\nu = \nu_v' - \nu_v = (\rho - 1)[(v' + \frac{1}{2})\omega_v' - (v'' + \frac{1}{2})\omega_v''],$$

where

$$\rho = \sqrt{\frac{\mu}{\mu_i}} \quad \text{and} \quad \omega_v = \frac{1}{2}[G(v + \frac{1}{2}) + G(v - \frac{1}{2})].$$

The vibrational quantum numbers which are the same for all bands in a row are given in column 1 of Table IV. The wave-numbers of the $\text{Se}_{78}\text{Se}_{80}$ heads and the observed and calculated values of $\Delta\nu$ are given in the second, third, and fourth columns respectively.

TABLE IV.—List of Isotope Heads.

1.	$\text{Se}_{78} \text{Se}_{80}$			$\text{Se}_{78} \text{Se}_{76}$			$\text{Se}_{78} \text{Se}_{80}$			$\text{Se}_{82} \text{Se}_{80}$		
	2.	3.	4.	5.	6.		7.	8.		9.	10.	11.
ν, ν'	ν	$\Delta\nu_{\text{obs.}}$	$\Delta\nu_{\text{calc.}}$	ν	$\Delta\nu_{\text{obs.}}$		$\text{Se}_{78} \text{Se}_{80}$ $\Delta\nu_{\text{calc.}}$	$\text{Se}_{78} \text{Se}_{76}$ $\Delta\nu_{\text{calc.}}$	ν	$\Delta\nu_{\text{obs.}}$		
21, 0	30731.6	22.2	22.0	30753.6	45.6		44.9	43.7				
20, 0	30357.2	22.6	22.3	30580.3	45.7		45.5	44.3				
19, 0	30370.9	20.9	22.5	30395.0	45.0		46.0	44.7				
18, 0	30175.7	21.4	22.0	30198.1	43.8		45.1	43.7				
17, 0	30001.2	20.5	21.1	30021.8	43.0		43.2	41.9				
16, 0	29777.2	21.3	20.3	29798.1	42.2		41.5	40.3		30135.0	19.3	21.1
15, 0	29570.1	20.5	19.2	29570.1	40.9		39.2	38.1		29933.4	20.5	20.8
14, 0	29359.7	17.9	18.3	29380.2	38.4		37.4	36.3		29732.4	22.5	19.4
13, 0	29147.2	18.2	17.2	29167.5	38.5		35.2	34.2		29528.8	20.8	18.4
12, 0	28930.2	13.8	16.1	28946.8	30.4		32.8	32.0		29318.9	22.9	17.5
13, 1	28763.1	14.7	14.8							29107.2	21.8	16.5
11, 0	28714.7	16.2	14.9							28901.3	15.1	15.4
14, 2	28593.0	13.0	13.3									
12, 1	28545.9	—	13.6									
13, 2	28375.7	9.2	12.3									
11, 1	28326.2	9.1	12.5	28344.7	27.6		25.5	24.8				
9, 0	28269.9	11.9	12.4									
14, 3	28208.5	11.0	10.9	28218.6	21.1		22.4	21.7				
10, 1	28118.7	11.5	11.1									
8, 0	28043.7	12.8	12.0	28057.0	26.1		24.6	23.8				
10, 2	27735.8	8.4	8.7	27748.6	21.2		17.8	17.3				

The positions of the heads due to $\text{Se}_{78}\text{Se}_{78}$ can be calculated from the known positions of the $\text{Se}_{78}\text{Se}_{80}$ heads. They lie within 1 cm.^{-1} of the positions calculated for the $\text{Se}_{76}\text{Se}_{80}$ heads. The observed head of shortest wavelength which falls in the calculated position must accordingly be a blend of these two heads. The wave-numbers and the observed values of $\Delta\nu$ are given in columns 5 and 6. The values of $\Delta\nu$ calculated for $\text{Se}_{76}\text{Se}_{80}$ and $\text{Se}_{78}\text{Se}_{78}$ are given in columns 7 and 8.

The faint head on the long-wave side is assigned to $\text{Se}_{82}\text{Se}_{80}$. As it lies within the strong head due to the main band, it is not favourably placed for measurement, and the agreement is accordingly not so good as in the other cases. The wave-numbers and observed and calculated values are given in columns 9, 10, and 11 respectively.

Summary.

The absorption band spectrum of Se_2 has been photographed and measured.

A vibrational analysis is given and large perturbations of the heads belonging to a number of levels have been found.

An isotope effect has been observed and good agreement is found between the observed and calculated positions of the heads.

In conclusion, I should like to thank Professor J. J. Nolan for his interest in the work.

References.

- (1) F. Diestelmeier, *Zs. f. Wiss. Phot.* xv. p. 18 (1916).
- (2) E. J. Evans and G. N. Antonoff, *Ast. Journ.* xxxiv. p. 277 (1911).
- (3) J. J. Fox and J. J. Dobbie, *Proc. Roy. Soc. A*, xcvi. p. 147 (1920).
- (4) B. Rosen, *Zs. f. Phys.* xliii. p. 69 (1927).
- (5) M. Moraczewska, *Zs. f. Phys.* lxii. p. 270 (1930).
- (6) E. Olsson, *Zs. f. Phys.* xc. p. 140 (1934).
- (7) Z. Bay and W. Steiner, *Zs. f. Phys.* xlv. p. 337 (1927).
- (8) See Jevons, 'Report on the Band Spectra of Diatomic Molecules,' p. 204.
- (9) Jevons, *loc. cit.*
- (10) F. W. Aston, *Proc. Roy. Soc. A*, cxxxii. p. 487 (1931).
- (11) J. Patkowski and W. E. Curtis, *Trans. Faraday Soc.* xxv. p. 725 (1929).

XXVII. *Viscosity and Heat Conduction according to the Geometrical Weight Method compared with other Treatments.* By W. S. KIMBALL, Ph.D., Michigan State College, East Lansing, Michigan *.

INTRODUCTION.

CONCERNING the idea of *differences* in distribution before, after, and between impacts, the question has been put :—"What more can be asked of a distribution than that it shall give the number of particles in each phase element?" The present paper attempts to answer this question by a comparison of the mechanical implications of the ellipsoidal and limaçonoidal distributions, on the one hand, with the mechanical implications of the viscosity and heat conductivity distributions of Chapman and Enskog and their followers, on the other. This comparison is made in the searching light of Maxwell's writings in their bearing on the special situations under consideration, *i. e.*, where a steady state independent of time prevails and yet the collision term of the continuity equation does not vanish. It is pointed out that Maxwell indicated that, in the absence of external forces, the collision rates of change would have to be balanced by molecular shifts of position arising from molecular speeds during time and space intervals *between* impacts, exactly as provided for by the ellipsoidal and limaçonoidal distributions. This latter rate of change Maxwell refers to as "the third way" by which changes in a phase element may take place.

Maxwell's writings afford three other surprising checks on the ellipsoidal and limaçonoidal distributions :—

(a) The ellipsoidal viscosity distribution, as a transient phenomenon for a given set of molecules, having pursued the ρ fractional part of their several free paths, was *exactly* anticipated by Maxwell, being relegated by him in general terms to a changing situation involving linear departures (homogeneous strain) from equilibrium conditions.

(b) Maxwell's "time of relaxation" is identified with the reciprocal of the equivalent impact frequency as

* Communicated by the Author.

used throughout the ellipsoidal and limaçonoidal distributions.

(c) The constant impact strain " a " of the strain laws for viscosity and heat conduction is identical with the constant collision strain that occurs during Maxwell's time of relaxation according to (14) and (35) below.

§1. When referring to all molecules per unit volume element of phase space, the ellipsoidal viscosity distribution function is an even function of all the velocity components with only second order departures from the Maxwell distribution.

The ellipsoidal * viscosity distribution may be written

$$f = \frac{1}{\alpha^3 \pi^{3/2}} \exp \left\{ - \left(\frac{c^2 + a^2 w^2 (2\rho - 1)^2 - 2auw(2\rho - 1)}{\alpha^2} \right) \right\} \\ = \left[\frac{1}{\alpha^3 \pi^{3/2}} \exp \left(\frac{-c^2}{\alpha^2} \right) \right] \left(1 + \frac{2auw(2\rho - 1) - a^2 w^2 (2\rho - 1)^2}{\alpha^2} + \frac{4a^2 u^2 w^2 (2\rho - 1)^2}{\alpha^4} \right), \quad (1)$$

indicating only the first and second order correction terms due to viscosity. When multiplied by $n d\rho$, where n is the molecular concentration, it gives, not the total number of molecules in unit six dimensional element of phase space, but merely the fraction of these having traversed the ρ -fractional part of their several free paths. Integrate out the variable ρ between the limits 0 and 1, and obtain

$$f = f_0 \left[1 + \frac{a^2 w^2}{3\alpha^2} \left(\frac{4u^2}{\alpha^2} - 1 \right) \right] \quad . \quad . \quad . \quad (2)$$

for the distribution function for *all* the molecules, regardless of the fraction ρ of free path traversed, that are included in unit six dimensional volume element in phase space. All the odd powers of u and w in (1) are multiplied by odd powers of $(2\rho - 1)$, which vanish upon integration with respect to ρ between limits 0 and 1. Hence (2) appears as an even function of the velocity components, and involves only second order departures from the Maxwell distribution. The amount of shear " a " is

* W. S. Kimball, Phil. Mag. xvi. p. 1 (1933).

of order 10^{-6} , so that (2) departs from the Maxwell distribution by terms whose order of magnitude does not exceed 1 part in a million million.

Eq. (2) illustrates how a distribution representing all the molecules per unit volume in phase space may refer by implication to a different distribution before, after, and between impacts, such explicit differences (indicated by (1)) having been removed by integration. Likewise, the distributions of Chapman * and Enskog † and Maxwell may, of course, refer to all the molecules per unit phase element including the distributions before, after, and between impacts.

It is the purpose of the present paper to point out certain requirements which must be met by all such inclusive distributions that apply to a *steady state* independent of time, especially where there is a *non-vanishing* collision term of the continuity equations, such as is the case with those of Chapman and Enskog, and recent extensions of their methods to the new statistics. These restrictions, be it noted, do *not* apply to Maxwell's distribution applicable to rarefied gases ‡, because it does not refer to such a steady state, but is subject to a time rate of decay and hence is outside the scope of the present article, being referred to only incidentally by way of comparison.

§ 2. Any viscosity distribution applicable to a steady state and referred to a frame moving with the gas that describes the shearing motion of all the molecules in a phase element between parallel planes, must be an even function of all the cartesian velocity components because of action and reaction.

Intermolecular forces and refinements which cause departures from the gas law and Maxwell's distribution, will also cause departures from the ellipsoidal distributions (1) and (2). There will still, however, be an equivalent "impact" shear of some kind, even though part of it is due to intermolecular force between the involved molecules shortly before and after "collision." It is very clear, however, that in case of a steady state independent of time, this forced "impact" shear—

* S. Chapman, Phil. Trans. Roy. Soc. 216 A (1916).

† D. Enskog, 'Inaugural Dissertation,' Upsala (1917).

‡ J. C. Maxwell, 'Scientific Papers,' ii. p. 693, eq. (21).

say in the negative x -direction—must be compensated, whatever its nature, by an equal and opposite positive shear, arising from “free” molecular trips from the place in the gas where the mass motion is positive. Accordingly, any molecule with velocity across the shearing planes will have the shearing motion imposed by impact as the predominant effect during the *first* half of its free trip, and during the last half a precisely compensating opposite effect (ruling out agitation velocity changes from consideration) due to molecular shifts of position *between* impacts. See fig. 3 of the *ellipsoidal viscosity* * *distribution*.

When we sum all these molecular groups along the free paths, the effects due to collision shifts and between impact shifts of position must balance and yield, for all molecules in a phase element at (x, y, z, u, v, w) an even distribution function like (2), when referred to a reference frame where the mass flow is zero. The argument here applies to shearing motion between parallel planes, regardless of intermolecular forces because, whatever their nature, these must act subject to action and reaction.

The argument of this section is strongly supported by Maxwell † in his treatment of stresses in rarefied gases, where he comments on “the third way in which variation of any quantity within an element may occur, namely, by molecules entering the element or leaving it, carrying their properties with them.” Accordingly, in case of viscosity where no external force field acts between impacts, the collision rates of change must be equal and opposite (in case of steady motion) to the rates of change of Maxwell’s “third way.” This latter is represented by the force equations (49) and (47) respectively in the case of the writer’s viscosity and heat conduction ‡ papers, being in each case the change due to free path shifts of position between impacts, which is Maxwell’s “third way,” being for both cases equal and opposite to the corresponding collision formulæ. Now in the special case of viscosity here treated these “third way” changes being equal and opposite to the collision changes (in the x -direction), it is clear that,

* Kimball, *loc. cit.*

† J. C. Maxwell, ‘Scientific Papers,’ ii. p. 696, § 7.

‡ W. S. Kimball, *Phil. Mag.* xx. p. 97 (1935).

according to Maxwell, we must have an even function of all the velocity components in case our distribution is to include velocities before, after, and between impacts, i. e., it is symmetric with respect to all three of the XYZ coordinate planes.

Now it will be noted that the distributions of Chapman and Enskog and the extensions of their methods to the new statistics do not show (when specialized for viscous shearing motion between parallel planes) the required symmetry with respect to each coordinate plane indicated by even functions of the cartesian velocity components, as is done by (2). Hence it is here contended that their distributions do not represent, as (2) does, all the molecules in a phase element for the steady motion as they purport to do, being for that purpose inconsistent with action and reaction.

§3. *The ellipsoidal velocity distribution applicable when strain variations take place in velocity space was exactly anticipated by Maxwell.*

In case of the ellipsoidal viscosity* distribution the standard form in cartesian velocity coordinates of the strain ellipsoid is

$$\frac{x'^2}{(c' \cot b)^2} + \frac{y'^2}{c'^2} + \frac{z'^2}{(c' \tan b)^2} = 1, \quad . \quad . \quad (3)$$

where b is the angle which the major axis of shear makes with the x -axis or direction of viscous flow. Here b is given in terms of the strain by

$$\cot b - \tan b = a(2\rho - 1). \quad . \quad . \quad . \quad (4)$$

Each member of (4) is the strain (the amount of shear) of the distribution, which varies from $-a$ to $+a$ as ρ , the fraction of free paths having been traversed by the molecules since last previous impact varies from zero to unity. Now solve (3) for c'^2 and substitute this for the c^2 appearing in Maxwell's familiar distribution law of spherical symmetry, and obtain

$$f(c^2) = \frac{1}{\alpha^3 \pi^{3/2}} e^{-\frac{c^2}{\alpha^2}} = \frac{1}{\alpha^3 \pi^{3/2}} \exp \left[- \left(\frac{x'^2}{(\alpha \cot b)^2} + \frac{y'^2}{\alpha^2} + \frac{z'^2}{(\alpha \tan b)^2} \right) \right], \quad . \quad (5)$$

which is the same identical ellipsoidal viscosity dis-

* W. S. Kimball, *loc. cit.*, see eq. (18) and fig. 7; and also eq. (85).

tribution function (1) above and given previously* in terms of polar and unsymmetric cartesian velocity coordinates. If we choose new constants, setting

$$\left. \begin{aligned} \alpha \cot b &= \alpha' \\ \alpha &= \beta' \\ \alpha \tan b &= \gamma' \end{aligned} \right\} \quad \alpha^3 = \alpha' \beta' \gamma' . \quad . \quad . \quad (6)$$

we have, instead of (5),

$$f(x'y'z') = \frac{1}{\alpha' \beta' \gamma' \pi^{3/2}} \exp \left[- \left(\frac{x'^2}{\alpha'^2} + \frac{y'^2}{\beta'^2} + \frac{z'^2}{\gamma'^2} \right) \right] . \quad (7)$$

Eq. (7) is a distribution identical to that given by Maxwell† as the "probable" one applicable to the case in hand. Maxwell's comment on its applicability is:—"When the differential elements of the gas are changing their figure, being compressed or extended along certain axes, the values of the mean square velocity will be different in different directions." The axes referred to can be nothing else than the principal axes of strain in velocity space, although the word "strain" is omitted. The other essential point in Maxwell's comment is that (7) refers, like (1) and (5), to a changing distribution; in that his "constants" $\alpha' \beta' \gamma'$ are subject to unspecified variations, which would include the changes in ρ and b of (1), (4), and (5), that represent the different distributions before, after, and between impacts. Thus Maxwell's suggested distribution (7) covers on its face all cases of homogeneous strain (since linear transformations yield a strain ellipsoid) in velocity space, being the first approximate departures from the spherical symmetry of the distribution known by his name. And it is striking that he should specify that it refers to changing configurations in velocity space, and only in such general terms as to make it cover the field and include the series of changing viscosity distributions indicated by (1) and (5).

§4. *When collisions take place in accord with Newtonian mechanics, the collision term of the continuity equation is zero, unless there is a distinction between the velocity distributions before and after impact.*

In case of viscous shearing motion in a gas between parallel planes, such as treated by the ellipsoidal viscosity

* W. S. Kimball, *loc. cit.*, see eqs. (21) and (81).

† J. C. Maxwell, 'Scientific Papers,' ii. p. 46, eq. (27).

distribution, there is, of course, an internal shearing stress which represents change of momentum involved in molecular collisions. Let the number of molecules per c.c. included in any particular velocity volume element $d\omega = du dv dw$ be given *before* impact by $dn = nf(u, v, w) d\omega$. Then the presence of the internal stress, due to molecular collisions, is proof (if Newtonian mechanics holds) that there will not be an equal number of molecules *after* impact in the same (any, particular) volume element $d\omega = du dv dw$ at (u, v, w) in velocity space. For, if such number is to be the same for each and every element $d\omega$, both before and after impact, then there can be no change (resultant or otherwise) of momentum upon impact (for the n -molecules per c.c. considered) and hence no such collision force as we know exists.

Furthermore, this internal stress is perhaps the most important manifestation of viscosity, so that this corresponding change of momentum involved in the distinction between the *before* and *after* impact distributions would seem also to be a most basic and important aspect of the viscosity distribution.

This argument applies with equal force to the case of heat conduction. For it is well known that the collision term of Boltzmann's equation (involving a collision force, *i. e.*, resultant rate of change of molecular velocity) is not zero except in case of the equilibrium* distributions of spherical symmetry, classical as well as recent. Collisions, accordingly, involve some kind of a resultant change of momentum, *i. e.*, difference in allotment of velocities to various velocity volume elements *before* and *after* impact, and this means that a *distinction* between the distributions *before* and *after* impact is required, except where equilibrium conditions prevail. This distinction, moreover, seems to be as essential to the problem as is the collision force itself and the collision term of the continuity equation.

As used here, the term impacts refers to equivalent impacts of negligible time duration, and velocities "before impact" apply when zero time and space intervals intervene previous to the next impact. And velocities after impact have an entire free path and corresponding time interval previous to the next impact.

* J. H. Jeans, 'Dynamical Theory of Gases,' eq. (24).

§ 5. *No single distribution for a steady state with non-vanishing collision term of the continuity equation can represent all the molecules in a phase element unless it is a sum or integral of a series of distributions, including those before and after equivalent impacts such as will represent whatever differences in distribution are required by the mechanics of collisions.*

If the foregoing argument is correct, it is not enough for a distribution function to give merely the total number (per unit volume) of molecules in volume element $d\omega = du dv dw$ of velocity space, as is done by those of Chapman and Enskog and the extensions of their methods to new statistics. For all such distributions, it still remains to be shown whether or not they include distinct distributions before and after impact, having these differences required by the dynamics of collisions in the Newtonian sense.

To make this point mathematically clear, turn to Jeans *, Chapter VIII., and his discussion of the collision term of Boltzmann's equation, and compare it with the treatment of viscosity by the geometrical weight method. The rate of increase, due to collisions, in the number of molecules per unit phase element is given † as the

product of $F' = \frac{w du_0}{dz}$ by $\frac{\partial(nf)}{\partial u}$. Let us equate this to Jeans's expression (517) for the same quantity

$$\begin{aligned} \iiint n^2(\bar{f}\bar{f}' - f\bar{f}')V du' dv' dw' p dp d\epsilon &= \frac{\partial nf}{\partial u} \frac{du_0}{dz} \cdot w \\ &= F' \frac{\partial nf}{\partial u} = \frac{\partial nf}{\partial u} \frac{w}{\lambda} \int \frac{2aw dn}{n} = \frac{\partial nf}{\partial u} \cdot \frac{w}{\lambda} \int 2aw f d\omega. \quad (8) \end{aligned}$$

The right-hand integral $\int 2aw f d\omega = 2a\bar{w}$, since it sums the product of the probability $f d\omega = \frac{dn}{n}$ times $2aw$, the

change of momentum (per unit mass) per impact due exclusively to viscosity. Note that this measures the mean value of the *change* in the distribution function when $u - aw$ before impact is replaced by $u + aw$ after

* J. H. Jeans, *loc. cit.* eq. (523). See also Maxwell, *loc. cit.* ii. p. 693, eq. (21).

† W. S. Kimball, *loc. cit.* eqs. (2), (88), (89).

impact, yielding the impact velocity difference $2aw$, due to viscous shearing impact force in the x -direction. Compare this with the *left* member, which uses the single distribution.

$$f=f_0(1+\Phi(x,y,z,u,v,w)) \quad . \quad . \quad . \quad (9)$$

to represent both the situations before and after impact indicated by dashes in the former case. The fact that dashes are used at all, however, indicates a difference between \dot{f} and \dot{f} obtained by inserting dashed velocities and otherwise in (9) for those before and after impact respectively. Thus the elements of Newtonian mechanics *i. e.*, velocity differences upon impact, are incorporated, at least formally, in the left member of (8). That it is correct to use a single distribution like (9) to represent a situation *both before* and *after* impact is clear, as is illustrated by Maxwell's law and (2) above. On the other hand, it is equally clear that under viscosity the distribution or grouping of molecules will not be the same *before* and *after* impact, as shown by section 4 and illustrated by (1) above. Accordingly, for a single distribution to include all, it will be necessary for it to be a summation of the various distributions before, after, and between impacts, such as is illustrated in section 1 above, where we carry (1) over into (2) by integration. Thus (9) must represent the result of this summation process and include a series of distributions like (1), including the *distinct* ones required by mechanics applicable *before* and *after* impact. Without such differences, implicit as in (2) or explicit as in (1), it will be inconsistent with the Newtonian mechanics of collisions. Not only so, but we may say that, as it stands, the basic mechanical characteristic of collisions in the Newtonian sense (impact change of momentum) is integrated out of (9) (if, indeed, it is a summation of the kind required), so that, like (2), it appears in a form from which the gist of the investigation has been removed by integration.

If these strictures upon (9) are well taken, certain limitations to its usefulness are to be expected. For example, how can the dynamics of collisions be incorporated into the collision term of Boltzmann's equation (the left member of (8)) by employing a single dis-

* Jeans, *loc. cit.* pp. 279-284. See also Maxwell, 'Scientific Papers,' ii. p. 40.

tribution function (9) from which the gist (the part representing impact change of momentum) of the Newtonian mechanics of collisions is already removed by integration? How could one use (2) the definite integral of (1) with impact changes (shown by the right member of (8)) obliterated by integration in the collision term of Boltzmann's equation, with any hope of obtaining a distribution showing the impact changes of (1) that characterize viscosity?

In this connexion recall that Maxwell used a single distribution only in two * cases: (a) where no change in distribution occurs before, after, and between impacts; (b) where the differences between the distribution before and after impact was not vital owing to the time-rate of decay of the distribution itself in a rarefied gas, which decay rate is itself the expression of collision reactions.

No matter how the dynamics of collisions † may be used to obtain such a distribution, it will, nevertheless, be inconsistent with Newtonian mechanics *unless* it is an integral or summation (like (2)) that includes two entirely distinct distributions indicated by (1) applicable before and after impact, and which provide for momentum changes according to the impact laws of Newtonian mechanics. This is just as certain as that collisions in the Newtonian sense are certain to cause *changes* of momentum upon impact, and that it is such changes that are represented by a non-vanishing collision term of the continuity equation.

Even when the collision term vanishes and the distributions before, after, and between impacts are alike, their sum or integral is still differentiable into the corresponding set of distinct distributions. Thus, Maxwell's familiar distribution law may be broken up in this way:

$$dn = \frac{n}{\alpha^3 \pi^{3/2}} e^{-\frac{u^2+v^2+w^2}{\alpha^2}} du dv dw d\rho = n f(uvw) d\omega d\rho. \quad (10)$$

This expression represents the number of molecules having pursued the ρ fraction (between ρ and $\rho+d\rho$) of their several equivalent free paths since last previous equivalent impact. That it is independent of ρ follows

* Maxwell, *loc. cit.* ii. pp. 44 and 691. (See also p. 351, where he treats the case of external forces.)

† Jeans, *loc. cit.*, see pp. 279-284; Maxwell, 'Scientific Papers,' ii. p. 40.

from the known and obvious aspects of this equilibrium distribution of spherical symmetry, which involves in its collisions identical expressions for action and reaction in each direction. If we integrate with respect to ρ from 0 to unity we include all the groups (10) as a summation in the familiar form

$$dn = \frac{n}{\alpha^3 \pi^{3/2}} e^{-\frac{u^2 + v^2 + w^2}{\alpha^2}} du dv dw, \quad \dots \quad (11)$$

which includes all the molecules at (u, v, w) in velocity space, regardless of whether they belong to the group at the beginnings or ends of their several free paths.

Accordingly the velocity distribution (11) is a sum or integral of the series of distributions (10), and includes those before and after impact required by the mechanics of collisions in the Newtonian sense. Likewise with the refinements of (11) given by the new statistics, which still refer to equilibrium conditions with identical distributions before and after impacts required by action and reaction, and the vanishing of the collision terms of the continuity equations.

§ 6. *Maxwell's writings indicate that he considered differences in velocity distribution before and after impact to be the gist of the theory.*

A derivation of Maxwell's law is to be found in vol. ii. p. 26, of his 'Scientific Papers.' On p. 45 he gives the law (26) and remarks immediately in the *same sentence*: "then this distribution of velocities will not be altered by exchange of velocities among the molecules by their mutual action." This indicates that change in distribution by the mutual action of molecules (upon equivalent impact) is *uppermost* in his mind, since the absence of such changes is put forward at *once* as the reason for the correctness of his law.

Likewise, on p. 351, he derives the law as modified by a force, having a potential such as gravity. The crucial step in his derivation is that whereby he justifies eq. (5). And he justifies this by the argument: "When the state of motion of the system is in its permanent condition, as many pairs of molecules change their velocities from V_1, V_2 to V_1', V_2' as from V_1', V_2' to $V_1 V_2$, and the circumstances of the encounter in the one case

are precisely similar to those in the second." The primed variables refer to *after* impact velocities and the unprimed variables to velocities *before* impact. The above quotation is a strong statement of the identity of the before and after impact distributions, and the whole derivation is shown to rest upon this crucial fact.

Maxwell is perhaps even more explicit when he treats stresses in rarefied gases (vol. ii. p. 681) where he employs Boltzmann's method. At the top of p. 690 he emphasizes the collision term shown as the left member of (8) above, "where f_2, f_1', f_2' denote what f_1 becomes when in place of the velocity components of M_1 before an encounter we put those of M_2 before an encounter, and those of M_1 and M_2 after an encounter respectively." In other words, the distribution functions f are not the same before and after encounters, but "become" something different as a result of collisions.

He then proceeds to calculate mean values for velocity combinations, using the special single distribution function (9) above according to Boltzmann (see his eqs. (12) and (21)), and referring to all the molecules within an element (see his p. 693, § 4). Hence the average values he obtains *include* velocities before, after, and between encounters, such as would be obtained by using (2) above to calculate averages.

The essential point about this treatment of Maxwell's is that it does *not* refer to "steady motion." Hence his mean values are subject to a rate of decay, and his eqs. (31) to (35) show the time-rate of change of the distribution function (9) itself.

Maxwell's reasons for not "attempting to enter into the calculation of the state of steady motion" (1st line, p. 702) are perhaps indicated in § 7, p. 696, where he points out that there are three ways in which any quantity within an element may vary. Apart from (1) encounters, (2) external forces, the third way is "by molecules entering the element or leaving it, carrying their properties with them." This comment indicates that he refers to what the writer has called changes of distribution due to free path shifts of position under uniform velocities (in the elementary case) during the time and space interval between impacts. Since Maxwell mentions only these three ways of change, the case of "steady motion" under *no* external forces will require this third

effect to exactly balance the collision effect. Thus Maxwell's point of view, here indicated, is exactly represented by the equal and opposite rates of change, F' and X' , given for the ellipsoidal viscosity * distribution by (2) and (49), and by the forces (44) and (47) for the limaçonoidal heat conductivity † distribution. The latter force in each case refers to molecules entering the element or leaving it, "carrying their properties with them," as Maxwell says. Accordingly, any attempt to portray viscosity by a single distribution (9) that has these essential differences (such as the impact differences noted by Maxwell in line 1, p. 690) removed by integration is beset with difficulty. In the unstable case, however, where Maxwell uses this single distribution to obtain averages, these differences in distribution play a less essential role, being absorbed by the rate of decay of the distribution itself; so that he obtains noteworthy results, though starting with a distribution function in which these differences are integrated out.

§ 7. *The distributions of Chapman and Enskog do not provide a non-vanishing collision term in the Newtonian sense, because they cannot be shown to include distinct distributions before and after impact, showing those differences required by the dynamics of collisions.*

It was noted in §2 above that, when specialized for the case of viscosity between parallel planes, the distributions of Chapman and Enskog do not show the symmetry with respect to the three cartesian coordinate planes required by any such viscosity distribution that is to include all the agitation velocities before, after, and between impacts. Let us examine the significance of this failure to meet the requirements of action and reaction. It means that these inclusive distributions cannot be shown to include such differences in distribution before and after impact as are required by the dynamics of collisions in the Newtonian sense, and explained in the last two sections. Accordingly, we conclude that the viscosity distributions of these authors do not provide for the continuity equations a non-vanishing collision term in the *Newtonian sense* that is

* W. S. Kimball, *loc. cit.*

† W. S. Kimball, *loc. cit.*

adequate to maintain the steady motion which they purport to describe.

Likewise, with the heat conductivity distributions of Chapman and Enskog and the extensions of their methods to the new statistics. These are shown in § 13 below to be of a form that cannot meet the requirements of equilibrium conditions, and a steady state involving maximum weight according to the equilibrium equations (31) below. Accordingly, they cannot provide a true collision term in the Newtonian sense, for the continuity equations, such as is required to maintain the steady states independent of time which they purport to describe.

The ellipsoidal viscosity distribution and limaçonoidal heat conductivity distribution, on the other hand, have completely preempted the situations which they purport to describe, and include precisely those differences in distribution before and after impact that have been shown to be unique and to fit the mechanics of collisions in every detail.

§ 8. *The distributions of Chapman and Enskog illustrate the flexibility of the mathematics in that they satisfy the requirements of continuity by providing a so-called "collision term," due to rates of change representing some new effect distinct from Newtonian collisions.*

It follows, however, from the non-vanishing of the so-called "collision terms," to which Chapman's and Enskog's distributions are applied, that they do provide a time-rate of change of velocity that purports to represent a collision force. On the other hand, their mathematics starts with a distribution (9), having collision differences already removed (see § 6 above) by integration. Furthermore, in spite of their employing impact laws *, such as developed by Maxwell, these are not incorporated into the distribution function so as to make it possible for it to include those distinct distributions, before and after encounters, that are required by collisions in the Newtonian sense.

What these authors have actually done, then, is to prove mathematically that a non-vanishing time-rate of change required by continuity is obtainable by solving

* Maxwell, *loc. cit.* vol. ii: p. 40.

the integral differential equation, under the assumption that each volume element in phase space has the same number of molecules before impact as after, since no change in distribution upon impact is provided for. Not only is it impossible to read into their distributions such required (in the Newtonian sense) changes as can be done for (2), but it is *unnecessary* to do so mathematically, because the non-vanishing integral term is provided for without them. Hence the non-vanishing collision term is taken care of by some non-Newtonian effect.

The true significance of their results, then, seems to be as an illustration of the flexibility of the mathematics by a demonstration that the needs of continuity can be taken care of without incorporating collision changes in the Newtonian sense, represented by impact changes of momentum and consequent inevitable corresponding changes in distribution before and after impact.

Accordingly, these distributions and their so-called collision terms are characteristic of some new effect distinct from Newtonian collisions and are at least of great mathematical interest, and, accordingly, are apt to find ultimately some valuable physical application in the future, but do not represent, it is here contended, the situations they purport to represent.

§ 9. *The constant impact shear of the viscosity shear law is the viscous shear during Maxwell's time of relaxation.*

Maxwell defines his "time of relaxation," t_1 , among other ways * by the formula

$$\eta = Et_1 = pt_1, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where η is the viscosity coefficient and $E = p = \frac{1}{2}\rho\alpha^2 = nkT$ is the elastic modulus or pressure. Maxwell also introduces (see footnote, p. 681, vol. ii. of his 'Scientific Papers') a "certain length" defined as the distance travelled under mean velocity during the time t_1 ,

$$\left. \begin{aligned} \lambda = ct_1 &= \frac{2\alpha}{\sqrt{\pi}} \left(\frac{\eta}{p} \right) = 2 \sqrt{\frac{2p}{\pi\rho}} \frac{\eta}{p} = 2\eta \sqrt{\frac{2}{\pi\rho p}}, \\ &= \frac{l}{1.178} = \frac{8l}{3\pi}, \end{aligned} \right\} \quad (13)$$

* Maxwell, *loc. cit.* vol. ii. pp. 30-32.

which indicates how this is related to the viscosity coefficient, pressure, and mean free path l .

Consider, now, a viscous shear between planes parallel to the xy -plane. We have $\frac{du_0}{dz}$ for the time-rate of shear,

where u_0 is the mass velocity of the gas. To find the amount of this shear during Maxwell's time of relaxation, we have the product

$$a = -t_1 \frac{du_0}{dz} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

If (12) is multiplied by $\frac{du_0}{dz}$ and (14) introduced, we have

$$p_{xz} = -\eta \frac{du_0}{dz} = -pt_1 \frac{du_0}{dz} = pa \quad . \quad . \quad . \quad (15)$$

for the shearing stress expressed in terms of the constant amount of shear during the time of relaxation, t_1 . Eqs. (12) to (15) be it emphasized are exclusively Maxwell's results taken direct from his works with nothing new added, save the constant amount of shear " a " during the time of relaxation, whose constancy (in velocity space) is as implicit in Maxwell's writings, as are its two explicit constant factors (14).

Now compare (13) to (15) with eqs. (1) and (91) of the ellipsoidal viscosity distribution. It will be noted that the relations are all identical. Accordingly, the constant impact shear of the viscosity shear law is identified with Maxwell's constant shear during his time of relaxation. Also the t_1 and λ of the ellipsoidal viscosity distribution are Maxwell's time of relaxation and corresponding length (13). Although λ was formerly referred to as a mean free path and the shear " a " as an "average shear," the special use made of these symbols indicates their identity with Maxwell's corresponding constants. The former is merely the reciprocal of the number of equivalent impacts per unit distance travelled, and the constant " a ," as used in the ellipsoidal distribution, is really the *viscosity* shear in contrast with shears due to the spherically symmetric random jumps involved in symmetric agitation velocities as such; *i. e.*, it is the shear represented by the non-vanishing collision term of Boltzmann's equation.

§10. *Maxwell's time of relaxation as applied to ideal gas is the reciprocal of the equivalent impact frequency.*

Maxwell's time of relaxation, given by (12) being, as applied to ideal gas, identified with the t_1 of (1) in the ellipsoidal distribution *, appears now as the reciprocal of the frequency of equivalent impacts, used in (1). Support for this interpretation is given by Maxwell implicitly in his treatment of stresses in rarefied gases †, where he gives his formulæ (31) to (35) for the time-rates of decay of the "constants" of the distribution function due to *collisions*. In each case these rates are proportional to $1/t_1 = p/\eta$, which he calls here the "modulus of the time of relaxation." That $1/t_1$ should be the number of collisions per second is, of course, in accord with this proportionality relation, assuming a given amount of decay per impact.

This identity for ideal gas between Maxwell's time of relaxation and the t_1 used as the reciprocal of equivalent impact frequency, rests on the general rule or principle ‡ heretofore found true, without exception for all cases treated by the geometrical weight method: *when any particular state of a gas involves stresses and strains in velocity space as well as ordinary space, the elastic modulus is the same for each space.* To show this refer to (91) of the ellipsoidal viscosity distribution,

$$p_{xz} = pa = \frac{\eta a}{t_1} = -\eta \frac{du_0}{dz} = -\eta \frac{dS}{dt} \quad . \quad . \quad (16)$$

In (16) note that p appears as the elastic modulus in *velocity* space connecting the shearing stress p_{xz} with the impact shear " a ," being the effective strain in velocity space. If p is to be the elastic modulus in ordinary space as required by the above capitalized principle, then, by Maxwell's definition of t_1 given by (12), we have

$p = \frac{\eta}{t_1}$ as indicated by the third member of (16), and the

right member is a matter of definition. Thus $1/t_1$ is required according to (16) to be the ratio of the time-

rate of shear $\frac{du_0}{dz}$ divided by the impact shear a , i. e., it is the impact frequency.

* Kimball, *loc. cit.*

† Maxwell, *loc. cit.* vol. ii. p. 681; see also pp. 695, 696.

‡ Kimball and Wygant, *Phil. Mag.* xix. p. 466 (1935).

A consideration of the unsteady state confirms this point. Thus, following Maxwell *, we write

$$\frac{dF}{dt} = \frac{dp_{xz}}{dt} = \frac{d(p_{xz} - pa)}{dt} = -\frac{1}{t_1}(p_{xz} - pa) = -\left(\frac{E - ET \frac{dS}{dt}}{T}\right). \quad (17)$$

The transient state indicated by (17) does not contemplate changes in pressure, temperature, or mass flow of the gas as a whole, so that $n_1 = \frac{1}{t_1}$ the number of impacts per second remains constant, and hence (16) is constant. Note how very special this situation is that defines t_1 . In the right member of (17) Maxwell sets the time-rate at which the difference $(p_{xz} - pa)$ disappears, *equal* (as well as proportional) to the product of this difference by the impact frequency (reciprocal of the time of relaxation). Multiply by t_1 and get

$$t_1 \frac{d(p_{xz} - pa)}{dt} = -(p_{xz} - pa). \quad (19)$$

The left member of (19) is the reduction per impact in the difference $(p_{xz} - pa) = F - ET \frac{dS}{dt}$, which is zero under steady motion, and the right member shows it as a 100 per cent. or complete reduction. Thus each equivalent impact provides a complete reduction to the steady state condition (16), and the time involved, being $T = t_1 = 1/n_1$ is thus, by definition, Maxwell's time of relaxation. The integral of (17) or (19) checks Maxwell's formula, using his notation

$$p_{xz} = pa + ce^{-n_1 t} = F = ET \frac{dS}{dt} + ce^{-\frac{t}{T}}. \quad (20)$$

Maxwell's appreciation of the fact that this time of relaxation for ideal gas is actually the reciprocal of the number of equivalent impacts per second is indicated by (13) above, where he shows the corresponding length to be slightly *smaller* than the mean free path. Thus, according to Maxwell, it takes somewhat *less* time for a gas to be reduced by process of collisions to steady motion according to (19) and (20), than for a molecule at average speed to pursue its mean free path length.

* Maxwell, *loc. cit.* vol. ii. pp. 30, 31.

But the *time* allotted to one *single* impact taken as the reciprocal of the impact frequency is the *minimum possible* time of relaxation required to measure the process of reduction to a steady state *due to collisions*. So the suggestion of (13) is that the time used up by a molecule at average speed during its *mean free path* length was discarded by Maxwell as of questionable significance, on account of various methods of averaging, whereas t_1 , given by (12) in terms of measurable physical quantities, affords a unique expression for impact frequency and time of relaxation. Fast molecules have higher impact frequency than slow ones, but the minuteness under ordinary conditions of the time of relaxation (average time interval between equivalent impacts) provides enough impacts to justify attributing this impact frequency $\left(n_1 = \frac{1}{t_1} = \frac{p}{\eta} = 10^{10}\right)$ to every similar molecule, each one having had plenty of time to go through the whole gamut of attainable velocities. It is a strong point in favour of the rigour of the ellipsoidal viscosity distribution that the impact frequency involved in its development is defined inadvertently (previous to 1935 the writer had never looked at Maxwell's 'Scientific Papers') in terms of such well determined quantities as Maxwell's time of relaxation and corresponding length λ travelled by a molecule at average speed. Accordingly, it is to be noted that the formulæ for the viscosity and heat conductivity coefficient, derived by the geometrical * weight † method, are actually expressed in terms of Maxwell's "relaxation length," given by (13) instead of the mean free path. This, of course, makes no difference in the crucial ratio discussed in § 14 below.

§ 11. *Chapman's inverse 5th power distribution specialized for viscosity between parallel planes, represents a constant shear like that of the shear law, which is the viscous shear during Maxwell's time of relaxation.*

When specialized for viscosity between parallel planes Chapman's inverse 5th power ‡ distribution is

$$f'(u, v, w) = f_0 \left(1 - \frac{1}{\pi n^5 A_1} \cdot \frac{10}{3\alpha^2} c_{31} u w \right), \quad (21)$$

* W. S. Kimball, *loc. cit.* eq. (93).

† W. S. Kimball, *loc. cit.* eq. (62)

‡ Chapman, *loc. cit.* p. 324.

where $f_0 = \frac{1}{\alpha^3 \pi^{3/2}} e^{-\frac{c^2}{\alpha^2}}$ is the familiar Maxwell law, and Chapman's hm is replaced by $1/\alpha^2$. Also, the indicated π is introduced and the 2 in front of c_{31} is removed from his (198) as corrections for misprints, so as to make his (198) agree with his (142). Here $c_{31} = 3 \frac{du_0}{dz}$ by Chapman's (72), since we here consider only the indicated viscous shear in the x -direction. Eq. (21) may be written

$$f' = f_0 \left(1 - \frac{10}{\pi n^5 A_1 \alpha^2} \frac{du_0}{dz} uw \right) = f_0 \left(1 + \frac{2a' uw}{\alpha^2} \right), \quad (22)$$

where

$$a' = -t_1 \frac{du_0}{dz} \quad \text{and} \quad t_1 = \frac{5}{\pi n_5 A_1}.$$

Here a' is defined as the viscous shear during the time t_1 shown by (26) below to be Maxwell's time of relaxation, in the form required by this distribution of Chapman.

We may compare (22) with the ellipsoidal distribution (1) immediately before impact where $\rho = 1$.

$$f = f_0 \left(1 + \frac{2auw}{\alpha^2} \right). \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Here the 2nd and higher powers of the amount of shear " a " are neglected, as having orders of magnitude not exceeding 10^{-12} . Eq. (23) may be used to check (91) of the original viscosity paper. Thus

$$p_{xz} = pa = \frac{1}{2} nm \alpha^2 a = \int maw^2 f d\omega = \int muw f d\omega. \quad (24)$$

The integrations can readily be performed using polar coordinates

$$\left. \begin{aligned} u &= c \sin \theta \cos \phi \\ v &= c \cos \theta \\ w &= c \sin \theta \sin \phi \end{aligned} \right\} d\omega = c^2 dc \sin \theta d\theta d\phi, \quad . \quad . \quad (25)$$

and it is noteworthy that the integration using aw^2 in the integrand checks identically that where uw is used instead*. The former case, however, represents the flux through unit area perpendicular to zz of impact

* Note the correction to eq. (95), Kimball, Phil. Mag. xvi. p. 1 (1933), in that (24) shows by symmetry that $p_{xz} = p_{zx}$, and hence the indicated zero for p_{zx} in the stress matrix (95) is an error, and so the Cauchy symmetry is explicit rather than implicit as formerly noted.

velocity increments in the x -direction $\Delta u = aw$, arising from the constant impact shear $a = \Delta u/w$, according to the viscosity shear law.

Now compare (22) with (23). Their similarity shows in view of (24) that (22) gives for the viscous stress

$$\left. \begin{aligned} p_{xz} &= pa' = \int ma'w^2 f' d\omega = \int m\Delta u w f' d\omega = \int muvf' d\omega, \\ &= -\frac{5kT}{\pi_5 A_1} \frac{du_0}{dz}, \quad \text{or} \quad \eta = \frac{5kT}{\pi_5 A_1} = mkTt_1 = pt_1. \end{aligned} \right\} \quad (26)$$

Here the indicated viscosity coefficient checks Chapman's formula (251) for the inverse 5th power. It also checks (12) above, which is Maxwell's formula that defines t_1 as the time of relaxation. Accordingly, the a' of (22) and (26) is proved to be the amount of viscous shear that occurs during Maxwell's time of relaxation as given by Chapman's distribution. Since one of the integrals (26) gives the flux of $m\Delta u = ma'w$ in the z -direction, it illustrates for Chapman's distribution (22) the point made in § 9 in connexion with the ellipsoidal distribution (23), *i. e.*, that the shear during the time of relaxation

$$a' = -t_1 \frac{du_0}{dz} = \frac{\Delta u}{w}$$

is a constant for all speeds and directions, and becomes the constant impact shear in case (22) is interpreted as a special distribution before or after impact like (23).

§ 12. *The necessary form of distributions for viscosity and heat conduction, when intermolecular forces are included according to the new quantum statistics.*

This section generalizes Theorem I of § 12 of the Ellipsoidal Viscosity Distribution, according to which equilibrium between stress and strain in velocity space is conditioned upon a distribution being of the *normal* law form in the velocity magnitudes—to the degree of accuracy of the gas law and Maxwell's distribution law—its two constants of integration $\lambda(\theta, \phi)$ and $A(\theta, \phi)$ being arbitrary functions of the direction angles in velocity space. This theorem is illustrated by the ellipsoidal viscosity distribution and the limaçonoidal heat conductivity distribution, each of which is free from velocity magnitudes except where these appear squared in the exponent, according to the requirements of the normal law.

When refinements such as van der Waals's forces, the Pauli exclusive principle, and the new statistics for repelling neutral or attracting molecules are considered, the geometrical expression * for weight is

$$W = N^N (r_1 r_1 \dots r_N) = N^N \frac{\left(1 \pm \frac{f_1}{A}\right)}{f_1} \frac{\left(1 \pm \frac{f_2}{A}\right)}{f_2} \frac{\left(1 \pm \frac{f_N}{A}\right)}{f_N} \quad (30)$$

We may maximize this by the Lagrange method for a constant energy $E(\theta, \phi)$ in any *particular direction*, i. e., keep angular variables in velocity space constant. Then the critical equations are

$$\left. \begin{aligned} &+W \frac{d}{dc} \log r_i + \lambda mc_i = 0 \\ \text{or } -\frac{W}{\lambda(\theta, \phi)} &= \frac{mc_1 dc_1}{dr_1/r_1} = \frac{mc_i dc_i}{dr_i/r_i} = -\frac{mc_i dc_i}{f / \left(1 \mp \frac{f}{A}\right)} \end{aligned} \right\} \quad (31)$$

which show how equilibrium between stress and strain in velocity space is maintained for each direction at a time. The integration of (31) introduces another arbitrary "constant" function of θ and ϕ

$$f(c, \theta, \phi) = \frac{1}{C(\theta, \phi) e^{-\frac{\lambda(\theta, \phi) mc^2}{2W} \pm \frac{1}{A}}}, \quad (32)$$

where $C(\theta, \phi)$ and $\lambda(\theta, \phi)$ are arbitrary (so far as (31) are concerned) functions of θ and ϕ , and which are to be determined for any particular case from the "boundary conditions" like the particular solution of any other differential equation whose complete solution involves arbitrary constants. Hence the Corollary to Theorem I., i. e.,

Formula (32) is the necessary and sufficient condition with accuracy corresponding to the expressions for weight of the new statistics, for maintenance of equilibrium between stress and strain for each direction, its two constants being arbitrary functions of the velocity direction angles.

The significance of (32), as the form of the general velocity distribution where mechanical equilibrium pre-

* Chandrasekhar, Phil. Mag. ix. p. 621 (1930).

vails, lies in the fact that it meets the requirements of Newtonian mechanics and elasticity theory under whatever laws of intermolecular force are taken care of by the expressions for weight in the new quantum statistics. That is to say, it *combines* the "accepted" manifestations of intermolecular forces according to the new statistics with the large scale stress strain requirements for mechanical equilibrium in each direction at a time of the geometrical weight method. This is in contrast to the way intermolecular forces are introduced by Chapman and Enskog. Eq. (32) thus points the way to a generalization of the new quantum statistics of Bose, Einstein, Fermi, and Dirac which will include those departures from spherical symmetry corresponding to viscosity and heat conduction. These would be the generalizations of the ellipsoidal viscosity distribution and the limaçonoidal heat conductivity distribution that are refined so as to include the departures of the new quantum statistics. Since the order of magnitude of molecular concentration is about 10^{19} , it is to be expected that distribution functions, describing as they do large scale relations, should have intermolecular forces introduced according to the experimental elastic relations of the new statistics according to the geometrical weight method, rather than by the microscopic detailed intermolecular force laws introduced by Chapman and Enskog.

§ 13. *The heat conductivity distributions of Chapman and Enskog, and the extensions of their method to the new statistics, are inconsistent with the requirements of Newtonian mechanics and elasticity theory for the equilibrium conditions of a steady state represented by maximum weight or entropy.*

When expanded in powers of c^2 , the viscosity distribution function (1), the limaçonoidal heat conductivity distribution *, or the extension (32) of these to include the intermolecular forces, etc., of the new statistics will all take the form

$$f(c, \theta, \phi) = a_0 + a_2 c^2 + a_4 c^4 + a_6 c^6 + \dots, \quad (33)$$

where the a 's are some functions of the angle variables

* Kimball, *loc. cit.*

θ , ϕ in *velocity* space. Note that only even powers of the velocity magnitudes are present, and that by (31) this is a consequence of the equilibrium ratios between *energy* differences and strains that represent maximum weight (30) or entropy. Furthermore, it will readily be seen that such a generalization of (31) as would result from using the relativity expression for energy would still result in a distribution expressible in even powers of c , as is included in (33). Likewise, if a more general expression for weight were used indicating a different law of intermolecular force* than those of the new statistics. Hence we conclude that (33) is the *necessary* form of a distribution that represents a steady state independent of time accompanied by viscosity or heat conduction, whether it refers to ideal gas or van der Waals's forces, other intermolecular forces or refinements of relativity and the new statistics. And this mechanical necessity arises from the need for equilibrium equations like (31) whenever a steady state is to prevail.

Now it is readily seen that the *heat conductivity* (this objection does not include viscosity) distributions of Chapman and Enskog and the extensions of their methods to the new statistics are all of them expansions in odd powers of the velocity magnitude c . Hence they all are inconsistent with (33) and the equilibrium equations like (31). Accordingly, they cannot represent a steady state independent of time such as is conditioned upon such equilibrium equations and as they purport to do, being for this purpose inconsistent with Newtonian mechanics and elasticity theory. We may illustrate by Chapman's general distribution function (142), which shows for heat conduction a series of even powered terms in c multiplied by u , v , or w , which are each given by (25) above in terms of the first power of c , and the velocity angle variables. Thus if we introduce (25) above into Chapman's eq. (142) we get for heat conduction a series in exclusively odd powers of c and for viscosity one in even powers of c (not included in the objections here discussed), each having coefficients dependent on the velocity angle variables. The former is impossible, since it is in disagreement with Newtonian mechanics according to (31) and (33) above. The same objection

* Kimball and Wygant, *loc. cit.*

is readily seen to apply with equal force to the heat conductivity distributions of Enskog *, Massey and Mohr †, Uhlenbeck and Uehling ‡.

On the other hand, this objection does *not* apply to the case treated by Maxwell § entitled "Stresses in Rarefied Gases." Although his formulæ (21) and (22) are expressed in odd as well as even powers of the velocity magnitude, yet they are only applied to a *transient* phenomenon such that the distribution function that describes it undergoes a rate of decay given by his formulæ (31) to (35). Accordingly, his distribution function is not subject to the restrictions imposed by equilibrium as given by (31) and (33). Furthermore, Maxwell shows in § 7 of this paper his appreciation of the conditions which must be met by any case of "steady || motion." He there comments on the "third way," besides collisions and a field of force, "in which a variation of any quantity within an element may occur, namely, by molecules entering the element and leaving it, carrying their properties with them." Now the immediate conclusion from this is that in case of "steady motion" and no force field, the "third way" must be equal and opposite to the collision method of variation of a quantity within an element. In accord with Maxwell's idea, the collision rates of change (2) and (44) given for viscosity ¶ and heat conduction** respectively by the geometrical weight are equal and opposite to the rates of change (49) and (47) method respectively in the viscosity and heat conduction papers, which latter formulæ indicate rates of change by Maxwell's "third way."

Other distributions, however, which, like those of Chapman and Enskog, are not included in (33), cannot represent equilibrium such as indicated by (31) and are in disagreement with Maxwell's idea of *equal* and *opposite* "variations of any quantity within an element" by collisions and by "the third way" respectively, such as

* Enskog, *loc. cit.*

† Massey and Mohr, Proc. Roy. Soc. cxli. p. 434 (1933); cxliv. p. 183 (1934).

‡ Uhlenbeck and Uehling, Phys. Rev. xxxix. p. 1014 (1932); xliii. p. 552 (1933); xlvi. p. 917 (1934).

§ Maxwell, *loc. cit.* ii. p. 693.

|| Maxwell, *loc. cit.* p. 702, line 1.

¶ Kimball, *loc. cit.*

** Kimball, *loc. cit.*

he indicates by implication are required where a steady state prevails.

§ 14. *The crucial ratio, $\epsilon = K/C_v\eta$ is too large by a 10 per cent. order of magnitude for those distributions whose correction terms are odd powered expansions having powers of C that are too large by unity.*

The limaçonidal heat conductivity distribution * just before impact when $\sigma = 2a$ may be expanded

$$\left. \begin{aligned} f(c, \theta) &= \frac{1}{\alpha^3 \pi^{3/2} b (1 + 2a \cos \theta)^4} = \exp \left(-\frac{c^2}{\alpha^2 (1 + 2a \cos \theta)} \right) \\ &= f_0 \left[1 - 8a \cos \theta \left(1 - \frac{c^2}{2\alpha^2} \right) \right] \\ &= f_0 \left[1 + \frac{8}{\sqrt{\pi}} \alpha \frac{t_1}{T} \frac{dT}{dx} \cos \theta \left(1 - \frac{c^2}{2\alpha^2} \right) \right] \end{aligned} \right\} \quad (34)$$

Here the second and higher powers of the strain constant “ a ” are neglected and $f_0 = \frac{1}{\alpha^2 \pi^{3/2}} e^{-\frac{c^2}{\alpha^2}}$, and in the right member we employ

$$-a = \frac{\lambda}{\alpha} \frac{d\alpha}{dx} = \frac{\lambda}{c} \frac{dc}{dx} = \frac{\lambda}{2T} \frac{dT}{dx} = \frac{\bar{c} t_1}{2T} \frac{dT}{dx} = \frac{\alpha t_1}{\sqrt{\pi} T} \frac{dT}{dx} \quad (35)$$

Eq. (35) gives the impact strain in terms of the temperature, time of relaxation t_1 and corresponding length λ according to (13) above and (59) of the previous * paper, and the changes in c indicated by (35) are temperature gradient changes due to collisions as distinct from random jumps according to (35) of the previous * paper.

If we set all the differential coefficients † in Chapman’s (198) equal to zero except $\frac{dT}{dx}$, we obtain his inverse 5th power distribution for the special case given by (34) above, and we introduce the t_1 of (22) shown above to be Maxwell’s time of relaxation

$$f = f_0 \left[1 + \frac{15}{4} \frac{t_1}{T} \frac{dT}{dx} u \left(1 - \frac{2}{5} \frac{c^2}{\alpha^2} \right) \right] \quad (36)$$

* Kimball, *loc. cit.*

† Chapman, *loc. cit.*

We may calculate the energy flux in the x -direction for each of these distributions (34) and (36) and compare

$$Q = \int \frac{1}{2} n m c^3 \cos \theta f d\omega. \quad . \quad . \quad . \quad (37)$$

Where $u = c \cos \theta$ and $d\omega = c^2 dc \sin \theta d\theta d\phi$. Integrate both the angle variables first and then there remains

$$Q_c = \frac{32}{3\pi} \left(\frac{p t_1}{\alpha^4 T} \frac{dT}{dx} \right) \int_0^\infty e^{-\frac{c^2}{\alpha^2}} \left(c^5 - \frac{1}{2} c^7 \right) dc = -\frac{64}{9\pi} C_v \eta \frac{dT}{dx}. \quad (38)$$

$$Q_c = \frac{5}{\sqrt{\pi}} \left(\frac{p t_1}{\alpha^5 T} \frac{dT}{dx} \right) \int_0^\infty e^{-\frac{c^2}{\alpha^2}} \left(c^6 - \frac{2}{5} c^8 \right) dc = -\frac{5}{2} C_v \eta \frac{dT}{dx}. \quad (39)$$

Here $C_v = \frac{3k}{2m}$ is the specific heat per unit mass and $\eta = p t_1$ is the viscosity coefficient by (12), and T is removed by $\frac{1}{2} m \alpha^2 = kT$. The numerical coefficient $\frac{32}{3\pi}$ in the left member of (38) is *larger* than $5/\sqrt{\pi}$ in (39), and yet (39) gives the crucial ratio $\epsilon = \frac{5}{2} = K/C_2 \eta$ between con-

ductivity coefficient and product of viscosity by specific heat, as about 10 per cent. larger than the crucial ratio $64/9\pi$ given by (38). This is because the indicated integral of the velocity magnitudes introduces a greater numerical factor $\left(\frac{3\sqrt{\pi}}{8} \right)$ in the second case than in the first $\left(\frac{1}{2} \right)$. This comparison indicates the mathematical

reason why (39) provides a larger crucial ratio than (38), *i. e.*, it follows directly from the fact that the distribution (36) has one higher power for the exponents of the velocity magnitudes in the correction terms than the limaçon distribution (34) does. Both of these distributions, of course, satisfy the elementary mass flow requirement $\int f c \cos \theta d\omega = 0$ which determines the factors $\left(1 - \frac{c^2}{2\alpha^2} \right)$ and $\left(1 - \frac{2c^2}{5\alpha^2} \right)$. But computation of the energy flux involving, as it does, higher powers of c , gives too much weight in case of (36) to velocities in the plus x -direction, so that this energy flux is 10 per cent. too large as given by (39).

Likewise with the other heat conductivity distributions of Chapman and Enskog and the extensions of their

methods to the new statistics. They all have velocity magnitudes in the expansions of their correction terms at powers that are too high by unity (odd powers). Hence they give like (39) too large an energy flux, and one inconsistent with the steady states which they purport to describe, and which can only exist when equilibrium eqs. like (31) are satisfied.

§15. *Chapman's inverse fifth power distribution for heat conduction in the x-direction represents a strain proportional to the velocity magnitude, but otherwise identical in form with the average strain of the limaçonoidal distribution.*

Let us calculate the form of the limaçonoidal distribution that represents at a given time *all* the molecules in a six-dimensional phase element including those before, after, and between impacts, as distinct from that which represents them only when the strain is σ , and they have pursued the ρ -fraction of their free paths. Instead of the latter case such as (34) when $\sigma=2a$ and $\rho=1$, we now have to integrate out the variable $\sigma=a(1+\rho)$. Thus

$$\left. \begin{aligned} \int_0^1 f d\rho &= \int_0^1 \frac{1}{\alpha^3 \pi^{3/2} b (1 + \sigma \cos \theta)^4} \exp\left(-\frac{c^2}{(1 + \sigma \cos \theta)^2}\right) d\rho \\ &= f_0 \int_0^1 \left(1 - 4a(1 + \rho) \cos \theta \left(1 - \frac{c^2}{2\alpha^2}\right)\right) d\rho \\ &= f_0 \left[1 - 4a\left(\frac{3}{2}\right) \cos \theta \left(1 - \frac{c^2}{2\alpha^2}\right)\right] \\ &= \frac{1}{\alpha^3 \pi^{3/2} \left(1 + \frac{3}{2}a \cos \theta\right)^4} \\ &\quad \exp\left(-\frac{c^2}{\alpha^2 \left(1 + \frac{3}{2}a \cos \theta\right)^2}\right). \end{aligned} \right\} \quad (40)$$

In the lower expressions we have neglected second and higher powers of impact strain $a = -\frac{\lambda}{2T} \frac{dT}{dx} = 10^{-6}$,

and we note that (40) is the same as the original limaçonoidal distribution with strain constant replaced by its arithmetic

mean $\frac{3}{2}a$ and b set equal to unity

The similarity of form shown by (34), (36), and (40) suggests the possibility of writing Chapman's distribution (36) above in the exponential form. Thus if we neglect second and higher powers of (35), we may write (36)

$$f = \frac{1}{\alpha^3 \pi^{3/2} \left(1 - \frac{3}{4} \frac{t_1}{T} \frac{dT}{dx} u\right)^5} \exp \left[- \frac{c^2}{\alpha^2 \left(1 - \frac{3}{4} \frac{t_1}{T} \frac{dT}{dx} u\right)^2} \right] \\ = \frac{1}{\alpha^3 \pi^{3/2} \left(1 + \frac{3ac \cos \theta}{2\bar{c}}\right)^5} \exp \left[- \frac{c^2}{\alpha^2 \left(1 + \frac{3ac \cos \theta}{2\bar{c}}\right)^2} \right] \quad (41)$$

where in the second expression we have introduced the constant temperature gradient strain (35) that occurs during Maxwell's time of relaxation. This distribution becomes negative for negative value of the variable c'

$$c' = \frac{c}{1 + \frac{3ac \cos \theta}{2\bar{c}}}; \quad dc' = \frac{dc}{\left(1 + \frac{3ac \cos \theta}{2\bar{c}}\right)^2} \quad (42)$$

The minuteness of (35), however, insures that this only occurs for values of c of the order of magnitude of the velocity of light. Hence this defect is harmless. If we employ the above c' instead of c together with θ and ϕ as variables and integrate with respect to c' from zero to infinity, using (41) in exponential form, it can be shown to satisfy all * of the elementary requirements (b), (c), (d), and (e) noted in § 2 in the previous † paper. Also, (41) gives for the energy flux and crucial ratio values identical with (39). By integrating c' instead of c in the interval zero to ∞ we restrict attention, of course, to positive values of (41).

It is to be emphasized that (41) differs from Chapman's inverse fifth power distribution (36) only by corrections (second and higher powers of a) whose order of magnitude does not exceed one part in a million million (since (35) is of the order of 10^{-6}). Hence its physical significance is of interest.

* These integrations give all exactly the same results as if (36) were used, except that the flux of momentum differs from $p = nkT$. by second and higher powers of " a ," as it does with the limaçon distribution.

† Kimball, *loc. cit.*

Note that under the transformations (42) for velocity magnitudes and for the solid angles

$$\frac{\sin \theta d\theta d\phi}{1 + \frac{3ac \cos \theta}{2\bar{c}}} = \sin \theta' d\theta' d\phi', \quad . . . \quad (43)$$

the distribution (41) transforms into Maxwell's law, representing spherical symmetry under no strain

$$dn = nfc^2 dc \sin \theta d\theta d\phi = \frac{n}{\alpha^3 \pi^{3/2}} \exp\left(-\frac{c'^2}{\alpha^2}\right) c'^2 dc' \sin \theta' d\theta' d\phi'. \quad . . . \quad (44)$$

Hence (41) may be taken to represent a strain in velocity space given by (42)

$$\frac{c-c'}{c'} = \frac{3ac \cos \theta}{2\bar{c}} = -\frac{3t_1}{4T} \frac{dT}{dx} u, \quad . . \quad (45)$$

which we see is proportional to the velocity magnitude c . And this is accompanied by the angular distortions (43).

The resemblance is very striking between Chapman's inverse fifth power distribution (41) and the limaçonoidal distribution (40), which is integrated so as to represent *all* the molecules in a phase element. It is easily seen that if the variable c in the strain (45) were set equal to its mean value \bar{c} , then (42) and (43) would simplify so as to transform Maxwell's law according to (44) directly into (40) instead of (41), with not even a change in numerical factors. Thus, except for this variable c instead of \bar{c} , Chapman has used the very same identical

"strain" $\frac{3a}{2}$, which is the strain of the limaçonoidal

distribution (40) when referring to all the molecules in unit phase element*, being expressed in terms of the constant impact strain, *i. e.*, the temperature-gradient strain " a " (35) during Maxwell's time of relaxation. Accordingly, *all* of the excess heat conduction (39) over (38) is to be attributed to the fact that (36) represents variable strain proportional to c , and hence gives an expansion in powers of c that are too big. Also, it is to be noted that if Chapman had used the strain constant $\sigma_1 = 2a$ (just before impact) instead of its mean

* This identity is formal, since Chapman's time of relaxation t_1 given by (26) is not the same as that given by (12), (15), and (35).

value $\frac{3a}{2}$, the excess of his heat conduction (39) over (38)

would have been that much greater, and all due to taking the strain (45) proportional to c instead of constant.

More detailed physical significance of (41) is obtainable by a comparison of its graph with that of (40), given by fig. 2 in the previous paper *. It will be seen that in view of (45), high velocities get more than their share of strain according to the requirements of Newtonian mechanics and the equilibrium equations for a steady state like (31). Hence (41), though of great interest mathematically, cannot represent a steady state independent of time maintained by Newtonian collisions.

§ 16. *Chapman's inverse fifth power distribution for this special case of heat conduction is an ellipsoidal distribution whose equal probability ellipsoids have their common focus at the origin.*

We may solve (42) for c and obtain the ellipsoid of revolution with focus at the origin

$$c = \frac{c'}{1 - \frac{3ac' \cos \theta}{2\bar{c}}}; \quad e' = \frac{3ac'}{2\bar{c}}, \quad . \quad . \quad . \quad (46)$$

and the indicated variable eccentricity. Eq. (46) shows that if c varies with θ so as to keep c' constant, i. e., refers to any point on one of the ellipsoids (46), then the probability involved in (44) is constant. Hence (46) are equal probability loci in velocity space obtained from the equal probability spheres of the Maxwell distribution by heterogeneous strain, given by

$$\left. \begin{aligned} \Delta u &= u - u' = u' \frac{3ac \cos \theta}{2c}, \\ \Delta v &= v - v' = v' \frac{3ac \cos \theta}{2c}, \\ \Delta w &= w - w' = w' \frac{3ac \cos \theta}{2c}, \end{aligned} \right\} . \quad . \quad . \quad (48)$$

which are the same as (42) where $c^2 = u^2 + v^2 + w^2$ and $c'^2 = u'^2 + v'^2 + w'^2$.

* Kimball, *loc. cit.*

Furthermore, the equation * for the circular lines of force in velocity space

$$c = \frac{c'}{\sin \theta'} \sin \theta, \quad . \quad . \quad . \quad . \quad . \quad (49)$$

applicable to the physical situation in hand, shows that when (42) or (46) above replaces c in (49) we get (43), taking † $d\theta = d\theta'$ and $d\phi = d\phi'$. Accordingly (42) and (43) indicate a strain along these lines of force (49).

When it comes to the forces themselves, however, Chapman's distribution (36) or (41) fails to meet requirements, for it does not represent maximum weight in each direction at a time, as required by Theorem I. of the previous paper ‡, nor are there any equilibrium force equations like (31) (above) to be found, which maximize the weight in each direction, and at the same time are the very forces calculated to distort a Maxwell distribution along the lines of force (49) into the distribution (41) with strains (45) and (47). Likewise, with the other distributions of Chapman § and Enskog || and the extensions ¶ of their methods to the new statistics **,.

On the other hand, the limaçonoidal distribution meets this exacting test †† in that the same identical force equations that (a) maintain maximum weight in each direction indicate the same rates of change (b) required to maintain continuity according to Boltzmann's equation, and (c) to distort Maxwell's law over into the limaçonoidal distribution.

§17. Conclusions.

1. The ellipsoidal viscosity distribution was *exactly* anticipated by Maxwell, who noted that it was "probably" applicable where strain variations take place in velocity space, such as have been shown to occur with steady motion under viscosity.

* Kimball, *loc. cit.* eq. (49).

† See the limaçonoidal distribution eqs. (50), (51), for a rigorous treatment of the actual situations, including second and higher powers of " α ."

‡ Kimball, *loc. cit.* eq. (31).

§ Chapman, S., *loc. cit.*

|| Enskog, D., *loc. cit.*

¶ Massey and Mohr, *loc. cit.*

** Uhlenbeck and Uehling, *loc. cit.*

†† Kimball, *loc. cit.* eqs. (4), (31), (32), (44), and (47).

2. Maxwell pointed out that in case of a non-vanishing collision term of Boltzmann's equation, there is a difference between the distributions before and after impact, and indicated appreciation that this difference is the gist of the problem.

3. Maxwell noted the kinematic time rate of change in a distribution *between* equivalent impacts due to molecular shifts from place to place where differences in temperature or mass flow exist. He referred to this as "the third way" by which changes take place "by molecules entering the element or leaving it, carrying their properties with them." In the absence of external forces, this "third way" must balance the "collision" way in case of a steady state as shown for the ellipsoidal and limaçonoidal distributions.

4. The consequence of this "third way" of Maxwell's is that for steady motion under viscosity between *parallel planes* any distribution that describes all the molecules in a phase element including those before, after, and between impacts, will be an *even* function (symmetric with respect to all three *xyz* coordinate planes) of all the cartesian components of agitation velocity (referred to a frame moving with the gas), this being required by continuity and action and reaction, including Maxwell's "third way" that counterbalances collisions. This *necessary* requirement holds for the ellipsoidal viscosity distribution but does not hold for the viscosity distributions of Chapman and Enskog, and the extensions of their methods to the new statistics.

5. The distributions of Chapman and Enskog and recent extensions of their methods to the new statistics illustrate the flexibility of the mathematics in that they provide a non-vanishing so-called "collision term" of continuity equations, due to rates of change arising from some new effect distinct from Newtonian collisions, since the impact changes in distribution required by the latter are not included, and which hence is not a real collision term at all.

6. The constant impact strain "*a*" of the viscosity shear law and the strain law for heat conduction is identical with the constant strain that occurs during Maxwell's time of relaxation.

7. Maxwell's time of relaxation as applied to ideal gas is the reciprocal of the equivalent impact frequency.

8. Chapman's inverse fifth power viscosity distribution, specialized for parallel plane motion, represents the constant shear during Maxwell's time of relaxation for the special case considered which becomes a constant impact shear, provided the distribution is taken to refer to the state of the gas *before*, or *after* impacts.

9. When intermolecular forces are included according to the new statistics, the distributions that maximize the weight in each direction, and hence represent the steady states under viscosity and heat conduction, take the form

$$f(c, \theta, \phi) = \frac{1}{C(\theta, \phi)e^{-\frac{\lambda(\theta, \phi)}{2W}mc^2 \pm \frac{1}{A}}},$$

giving always expansions in exclusively even powers of the agitation velocity magnitudes (referred to a frame at rest in the gas).

10. The *heat conductivity* distributions of Chapman and Enskog and recent extensions of their methods by Massey and Mohr, Uhlenbeck and Uehling are all expansions in odd powers of the agitation velocity magnitudes and hence cannot represent steady states unvarying with time as they purport to do. This objection does not, of course, apply to Maxwell's *varying* distribution for rarefied gases, nor to the viscosity distributions of the authors, which latter are expansions in even powers of the velocity magnitudes.

11. Chapman's inverse fifth power distribution for heat conduction in the x -direction is expressible exponentially (to a high approximation) as an ellipsoidal distribution, having confocal strain ellipsoids (equal probability ones) derived from the equal probability spheres of the Maxwell distribution by heterogeneous strain *proportional to c* and with common focus at the origin. And this strain $\frac{3ac \cos \theta}{2c}$ becomes (formally)

when c is replaced by its mean value \bar{c} , the very identical average strain $\frac{3a \cos \theta}{2}$ of the limaçonoidal distribution

when integrated so as to include all molecules before, after, and between impacts together. Thus Chapman's distribution is completely transformed into this integrated

form of the limaçon distribution of average strain, in terms of the strain constant " a ."

12. Accordingly, the heat conductivity for this ellipsoidal distribution of Chapman (identical with that for his eq. (198)), as well as his crucial ratio $\bar{K}/C_v\eta = \frac{5}{2}$,

is too large by 10 per cent., and this excess is shown to result *solely* from the fact that its expansion is in powers of c that are once too large (odd powers), i. e., from the single fact that the strain of his ellipsoidal distribution is proportional to c instead of independent of this velocity magnitude as required by the heat conductivity strain law for the case in hand, being the *constant* collision strain that occurs during Maxwell's time of relaxation.

13. Likewise, the other heat conductivity distributions of Chapman, as well as of Enskog, Massey and Mohr, Uhlenbeck and Uehling, being expansions in powers of c that are once too big, give too large a crucial ratio by virtue of the fact that these odd power expansions do not represent the steady states which they purport to describe.

14. The basic inadequacy, however, in all these treatments is that they begin with a single inclusive distribution from which the gist of the problem (impact changes of momentum involved in Newtonian collisions that require *different distributions* before and after impact) is excluded at the start and kept out by their modes of treatment. For no single inclusive distribution for all the particles in a phase element can represent Newtonian collisions unless it is a summation or integral that includes distinct distributions before and after impact, differing in such a way as to meet the appropriate collision requirements of:—

(a) Equilibrium between stress and strain in velocity as well as ordinary space.

(b) Conservation of energy.

(c) Action and reaction.

(d) Equilibrium of torques.

(e) Equipartition of energy.

(f) Persistence of velocities.

15. Furthermore, the force expressions that meet these collision requirements (a) to (f) above must be the very same forces that represent the rates of change of the collision terms of the continuity equation.

These requirements are all met by the ellipsoidal viscosity distribution and the limaçonoidal distribution, whereas, none of the distributions of Chapman, Enskog, and recent * extensions of their methods † have been shown to meet *any* of them, and it is the contention of the present paper that it is quite impossible for these distributions to meet these requirements of the dynamics of collisions as indicated in paragraphs 4, 9, 10, 12, 13, and 14 of these conclusions.

XXVIII. *The Optical Constants of the Copper-Nickel Alloys.*

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I. *Introduction.*

IN a research aiming at the determination of the optical constants (the refractive index n , the absorption coefficient K , and the reflexion coefficient R) of complex binary alloys through as wide a wave-length range as possible, with a view to their correlation with crystalline structure, the copper-nickel system offers distinct advantages as a starting-point.

(i.) The alloys of the system form a continuous series of solid solutions ⁽¹⁾, in which the metals unite in all proportions, each alloy being a single homogeneous phase. The physical properties of such a series, for example, the electrical ⁽²⁾ and thermal ⁽³⁾ conductivities, and thermo-electric ⁽⁴⁾ power show continuous but non-linear variations from one end of the series to the other. It is to be expected, therefore, that the optical constants should also vary continuously. There cannot be any abrupt changes from one specimen to the next.

* Massey and Mohr, *loc. cit.*

† Uhlenbeck and Uehling, *loc. cit.*

‡ Communicated by the Authors.

This provides a good test of the technique employed, for all the points obtained experimentally should lie on a smooth curve. It is important to notice that for the term "optical constant" to have any meaning, the alloy must be either a solid solution or a compound. A two-phase alloy must necessarily consist of separate microscopic particles lying side by side, whose optical properties bear no relation to each other, and which reflect light independently of each other. Such an alloy can be examined optically (see later), and data can be obtained from which optical constants may be calculated. Obviously such constants have no physical significance. Solid solutions and compounds, however, are equivalent to pure metals. They consist of one phase only. Microscopically they are indistinguishable from a pure metal. They are atomically homogeneous. It follows that the optical constants of such alloys have the same physical interpretation as those for pure metals.

(ii.) Both copper and nickel have face-centred cubic lattices of almost identical size. For copper, the lattice constant $a = 3.60 \times 10^{-8}$ cm.; for nickel, $a = 3.54 \times 10^{-8}$ cm., the alloy, in which the copper and nickel atoms are completely interchangeable having a unit cube whose length varies linearly with atomic concentration ⁽⁵⁾. Experiments on single crystals ⁽⁶⁾ have shown that hexagonal metals such as zinc, magnesium, etc., have two sets of optical constants according as the axis is parallel or perpendicular to the reflecting surface, whereas cubic crystals have only one set. A polycrystalline surface of these uniaxial crystals yields an "average" value for the optical constants, whereas a polycrystalline surface of cubic crystals, *e. g.*, copper and nickel, yields true values for the particular surface under investigation. A similar argument applies for the copper-nickel alloys. The complication of working with alloys consisting of cubic and hexagonal components is avoided.

(iii.) Copper has an absorption band in the visible region. This results in the optical constants of copper and nickel being very dissimilar, so that in the alloys a large variation through the series may be expected, while the shift of the absorption region as the nickel is added in increasing proportion to the copper may be studied.

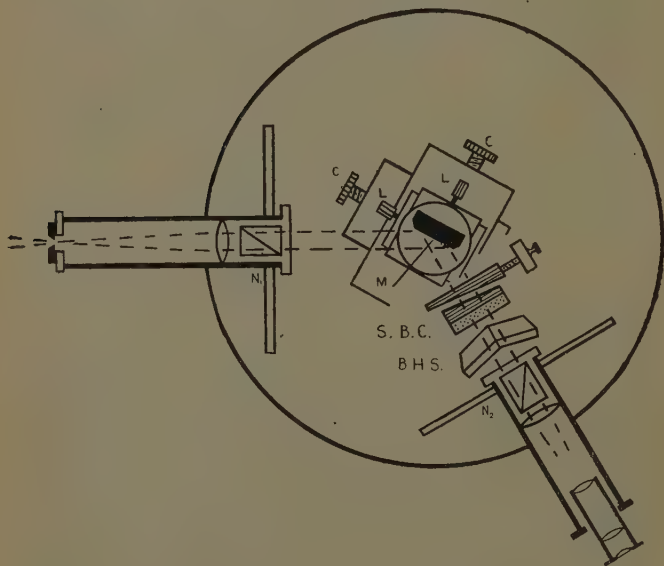
II. Experimental.

(i.) Measurement of Optical Constants.

The apparatus proper consisted of a Fuess No. 1 A Goniometer-spectrometer, a complete description of which is given in Tutton's 'Crystallography.' A Hilger monochromator, illuminated by a mercury-vapour lamp, supplied monochromatic light of wave-lengths 5780 \AA.

Fig. 1.

GONIOMETER



5461 \AA. , and 4358 \AA. By means of the goniometer-collimator and a Glan-Thomson polarizing Nicol, N_1 , a parallel beam of light, polarized at an azimuth of 45° , was incident on the polished polycrystalline plane surface of the alloy, M (fig. 1). The reflected elliptically polarized light was analysed by the Soleil-Babinet compensator, S.B.C., which measured the phase difference between the components parallel and perpendicular to the incident plane, and the analysing Glan-Thomson

Nicol, N_2 , combined with the Biplate Half-Shade, B.H.S., which measured the azimuth ψ of the restored plane-polarized light. The following equations derived from Drude were used in the computations :—

$$\tan Q = \sin \Delta \cdot \tan 2\psi,$$

$$\cos 2P = \cos \Delta \cdot \sin 2\psi,$$

$$S = \sin \phi \cdot \tan \phi \cdot \tan P,$$

$$A = S^2 \cdot \cos 2Q + \sin^2 \phi = n^2 - K^2,$$

$$B = S^2 \cdot \sin 2Q = n^2 + K^2,$$

$$2n^2 = \sqrt{A^2 + B^2} + A,$$

$$2K^2 = \sqrt{A^2 + B^2} - A,$$

$$R = \frac{n^2 + K^2 + 1 - 2n}{n^2 + K^2 + 1 + 2n},$$

where

ϕ = angle of incidence,

n = refractive index,

K = absorption coefficient,

R = reflexion coefficient.

Note that $K = nk$ where k = extinction coefficient.

Complete extinction of the reflected light by combined adjustments of the compensator and analyser could never be obtained, but only a minimum of intensity together with a non-homogeneous field, probably caused by some fault in the quartz of the compensator.

The accuracy of the mean observations both for Δ and ψ , however, was still about $\frac{1}{4}$ per cent., which was quite sufficient for the measurements involved.

The half-shade was made from good strain-free microscope slides, one edge ground and bevelled with a template to an angle of 60° , cut into pieces 1.3×1.0 cm. and cemented together along the bevelled edge. The common edge was adjusted to be perpendicular to the plane of polarization of the analysing Nicol and in use is rotated through a suitable angle about an axis perpendicular to the common edge and to the direction of the incident light. An account of a similar arrangement is given by C. V. Kent ⁽⁷⁾. It has the advantage that the half shadow angle is variable over a very wide range, a matter of importance when complete extinction is not obtained.

In taking observations at a particular wave-length, the specimen was placed on the rocking table and its position adjusted by the centring and levelling screws, until it was in the centre of the field of view for all angles of incidence on both sides of the zero position. The telescopic eyepiece was used for these observations. The compensator and analyser were then adjusted together, using the microscopic eyepiece, to give minimum intensity, the angle of incidence used being such that Δ was approximately 90° . Drude ⁽⁸⁾ has shown that the errors of observation are least for this position. Ten compensator readings were taken, followed by ten analyser readings. The polarizing Nicol was then rotated through 90° , and the two sets of readings repeated. The complete procedure was then repeated for the same angle of incidence to correct for any centring errors of the specimen, and for incorrect alignment of the collimator and telescope. Finally, a set of ten readings of the compensator for the zero position with the specimen lowered out of the path were taken. The whole series of observations for one wave-length took about twenty minutes. The difference between the analyser readings for the two positions of the polarizing Nicol, N_1 , gave 2ψ , whilst from the difference between the compensator readings for the direct and the reflected beams, Δ was calculated.

(ii.) *Preparation of the Alloys.*

Preliminary attempts at melting in the open air having proved unsuccessful, due to copper-oxide inclusions, a high frequency vacuum induction furnace was employed with good results. Electrolytic copper of 99.98 per cent. purity was used. This was cut into assorted sizes for convenience in weighing and cleaned with acid. The Mond Nickel Company kindly supplied the nickel shot, in different sizes, with an analysis of 99.94 per cent. from their research laboratories. To prevent possible contamination of the alloys, weighed quantities of the metal were placed in a Morgan "B" crucible lined with alumina ⁽⁹⁾.

As the vacuum apparatus was not good enough to prevent electrodeless discharges inside the silica vacuum tube ⁽¹⁰⁾, melting was finally carried out under a steady stream of purified hydrogen at a pressure of 6 cm. This

effectively prevents discharges and reduces any oxides that might be present, while any gases evolved from the metal on heating and ingress of air due to leakage would be swept away. When both the copper and nickel had melted, the mixture was kept molten for a few minutes to ensure thorough mixing by electromagnetic stirring. The enclosure was then evacuated, and during a period of 10-20 minutes the alloy was kept in a pasty condition by switching the furnace on and off for short bursts. This treatment ⁽¹¹⁾ allows bubbles of liberated gas to escape from the metal, thus minimizing the chance of blowholes or pinholes being formed. When solidification had occurred, the alloy was inverted in the crucible and the whole process repeated, in order to produce more perfect homogeneity. About half the alloys so prepared proved on examination to be satisfactory. Of these, twelve were selected for further preparation. They were analysed by estimation of the nickel content by the glyoxime method, which tests showed to be correct to one part in 200.

(iii.) Preparation of the Mirrors.

The standard metallurgical method of preparing a surface sufficiently plane for the purpose was adopted. The alloys were first sawn to shape with a hacksaw, rubbed flat against a file, and ground to "0000" emery. When using the fine French papers, "00" to "0000," the intrusion of coarse particles producing deep scratches could only be prevented by frequent washing of the hands, the use of paraffin as a lubricant, and constant rinsing of the paper with methylated ether. The specimens were then polished and examined under the microscope. All, except copper and nickel, showed a cored structure ⁽¹²⁾ characteristic of isomorphous alloys arranged in a dendritic pattern of width about 60μ . They were made homogeneous by annealing in an evacuated electric wire-wound silica furnace, at a temperature not far below melting-point (the higher the temperature the greater is the speed of diffusion) ⁽¹³⁾, and cooled very slowly (over a period of about eight hours) to 500°C . Periodic annealing and examination were continued until the crystal grains now observed (the coring had completely disappeared) were, as far as could be seen under a magnification

of 450 times, perfectly homogeneous. Table I. shows the total heat treatment received.

This treatment agrees with the results of Bruni and Meneghini⁽¹⁴⁾, who required proportionate times and temperatures to produce complete diffusion of copper with nickel, the copper being deposited as layers on nickel wires.

It is interesting to note that at 1100° C. a steady vacuum of 10^{-3} cm. was obtained but could not be improved, whereas in the annealing at 750° C. a pressure too low to be measured by a McLeod gauge (approx. 10^{-6} cm.) could be reached.

The production and growth of the crystals by this prolonged annealing produced a rough surface due to regrowth of crystals which necessitated regrinding on the Fench papers from "0" to "0000." The subsequent surface cold work was removed by bright-annealing each specimen *in vacuo* for three hours at 750° C., a treatment which, as shown by the work of Kirk Rose⁽²⁸⁾, was quite adequate, after which, with a final treatment on the "0000" paper, they were ready for the polishing process.

(iv.) *Polishing.*

The polished surface undoubtedly produces the greatest uncertainty in the values of the optical constants obtained by different workers, both through the variety of methods used in preparing the surface and through the unavoidable variations in technique and manipulation of a single observer. The nature of the surface layer, with which we are intimately concerned, has been the subject of many investigations. The weight of evidence lends support to Beilby's⁽¹⁵⁾ amorphous layer hypothesis. His exhaustive experiments led him to the view that the surface layer of polished substances was not crystalline, like the interior, but amorphous. The atoms are not arranged in any crystalline pattern, but are distributed at random like the molecules of a liquid, due perhaps to local high temperatures⁽¹⁶⁾ imposing a temporary mobility on the surface atoms. The electron diffraction experiments of G. P. Thomson⁽¹⁷⁾, and those of Finch, Quarrel, and Roebuck⁽¹⁸⁾ apparently leave no doubt as to the reality of the Beilby layer.

Since the optical constants depend not only on the

TABLE I.

Atomic percent. nickel.	0	8.8	18.4	24.7	35.2	45.1	53.2	64.9	76.0	85.5	91.8	100
30 hours at 950° C. ...	×	×		×			×					×
17 hours above 1000° C. including 13 hours at 1100° C.			×		×		×		×	×	×	
50 hours at 1100° C. ...		×			×	×	×	×	×	×	×	
74 hours at 1030° C. ..				×								

" × " indicates the treatment received.

properties of the atoms themselves, but also on their arrangement (as the experiments on single crystals ⁽⁶⁾ confirm), the possible effect of this film on the optical properties of the metal becomes of great importance. The experiments of Beilby on copper films, and the results of electron diffraction, suggest that an ordinary polish must consist of an amorphous layer 20-50 atoms thick, while this must be greatly exceeded by heavy polishing using rouge or a burnishing tool. Taking this figure, Blackman ⁽¹⁹⁾, in a theoretical investigation, concludes that it would have a negligible effect in the infra-red, but would affect the ultra-violet. Experiments show that a heavy polish definitely affects the optical constants both in the ultra-violet ⁽²⁰⁾ and the visible ⁽²¹⁾ region, while according to Mott and Zener ⁽²²⁾, the poorer conducting surface layers should also affect results in the infra-red. It is evident, then, that if a close approximation to the actual optical constants of the bulk material is required, as thin a surface layer as possible must be aimed at. This rules out the burnishing methods of Drude, Tool ⁽²³⁾ and others, and the use of rouge, which not only produces a heavy flow, but also contaminates the surface ⁽²⁴⁾. Magnesia, owing to its fine and uniform quality, and to its abrasive as well as polishing action, has been used. Polishing was carried out in the following stages :—

(1) The specimens were held lightly against a damp "Selvyt" polishing cloth stretched over a rapidly rotating brass disk, and covered with a paste of finely divided magnesia and distilled water. This very quickly removed the "0000" scratches and left a highly polished surface marred by very fine "wheelmarks." The surface was then carefully etched with standard acid ferric chloride diluted with its own volume of water to remove the amorphous layer, until the crystal boundaries were just visible under the microscope. This sometimes revealed scratches which had been buried under the surface layer, in which case alternate etching and polishing were helpful in removing them.

(2) A little of the magnesia powder was shaken in distilled water, and after standing for five minutes the suspension was poured on to a clean cloth and polishing carried out with the wheel rotating slowly until all

"wheelmarks" had been removed. It was then etched as before very carefully, but with very dilute solution, since the layer after this process was very thin.

(3) Final polishing was done by hand, with a ten-minute suspension of magnesia, the cloth being stretched tightly over a piece of plate glass. Where difficulty was experienced in removing very fine scratches, rubbing the specimen on the palm of the hand moistened with a trace of magnesia was found highly successful. Elimination of these fine scratches is essential, for Drude⁽⁸⁾ has shown that uniform scratches alter the values of the optical constants. Any grease was removed by absolute alcohol, and finally the surface was well washed in running water, carefully dried, and immediately measured.

Preliminary work showed that repeat values of the optical constants for a single specimen might vary by as much as 15–20 per cent. from each other, and in working out the method of polishing described whereby these discrepancies might be minimized, Tool's⁽²⁵⁾ observation that a matt surface or incomplete polish reduces the values of the optical constants was confirmed. A great deal of practice and constant experience were necessary before the technique of producing satisfactory surfaces for the purpose of measurement was perfected. Only by striving for a completely polished surface (consistent with as thin a flowed layer as possible), and confirmed by the approach of the values of the constants to a maximum as polishing attained perfection, was it possible to obtain consistent results. In the final state of the surface, scratches and wheelmarks were almost completely eliminated, the surface proper could not be focussed under the microscope, and when illuminated with oblique light in a dark room the scattered light was so small that the surface was invisible.

The tables give the values of the three final consecutive determinations for each alloy, the surface being independently prepared each time. It will be seen that for any alloy they are, in general, well within 5 per cent. of the mean values.

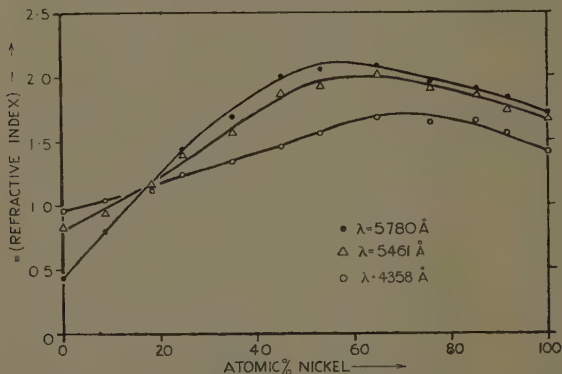
In view of the fact that these variations of optical constants have been known for some time⁽²⁵⁾, it is rather surprising that nearly all quoted results of optical constants of metals and alloys give the values of one observation only.

It appears that, if results are to have any value, at least three concordant values for each specimen are required.

III. Discussion of Results.

The mean values of n , K , R , nK , and $n^2 - K^2$, derived from the data in Tables II.-IV., are shown in figs. 2-6, plotted against the atomic composition of the alloys for the wave-lengths 5780 Å., 5461 Å., and 4358 Å. nK_ν corresponds to the electrical conductivity for frequency ν , whilst $n^2 - K^2 = \epsilon$ the dielectric constant for this frequency. ϵ is always negative for metals.

Fig. 2.



The curves show a continuous but non-linear variation in the values of all the constants throughout the series. The n and nK curves have maxima for each wave-length at the same composition, the positions varying from about 55 per cent. for the yellow to 70 per cent. for violet. The K curve rises steeply from copper to maximum values at approximately 35, 45, and 60 atomic per cent. nickel for the three wave-lengths. For the yellow and green wave-lengths, minimum values of K occur at about 65 per cent., after which they rise again to their highest values for nickel. The $n^2 - K^2$ curve shows similar minima and maxima, but in a much more pronounced form and for all three wave-lengths. The minima occur at about 25, 30, and 50 per cent., and maxima at 60, 65, and 85 per cent.

TABLE II.

Optical Constants of Copper-Nickel alloys. $\lambda=5780 \text{ \AA}$.

Atomic percent. nickel.	ϕ .	Δ .	2ψ .	n .	K .	Means. n K .		R. percent.	nK .	$n^2 - K^2$.
	$^{\circ}$	$^{\circ}$	$^{\circ}$							
0 ... 71	0	$\left\{ \begin{array}{l} 82 \ 41 \\ 88 \ 27 \\ 88 \ 39 \end{array} \right.$	$\left\{ \begin{array}{l} 80 \ 31 \\ 82 \ 7 \\ 80 \ 43 \end{array} \right.$	$\left\{ \begin{array}{l} 0.437 \\ 0.392 \\ 0.463 \end{array} \right.$	$\left\{ \begin{array}{l} 2.20 \\ 2.48 \\ 2.48 \end{array} \right.$	0.431	2.39	77.8	1.03	-5.53
8.8 ... 71	0	$\left\{ \begin{array}{l} 93 \ 55 \\ 97 \ 20 \\ 95 \ 30 \end{array} \right.$	$\left\{ \begin{array}{l} 74 \ 35 \\ 76 \ 4 \\ 65 \ 45 \end{array} \right.$	$\left\{ \begin{array}{l} 0.825 \\ 0.791 \\ 0.785 \end{array} \right.$	$\left\{ \begin{array}{l} 2.68 \\ 2.88 \\ 2.78 \end{array} \right.$					
18.4 ... 73	15	$\left\{ \begin{array}{l} 97 \ 13 \\ 97 \ 20 \\ 96 \ 34 \end{array} \right.$	$\left\{ \begin{array}{l} 72 \ 23 \\ 72 \ 7 \\ 72 \ 18 \end{array} \right.$	$\left\{ \begin{array}{l} 1.14 \\ 1.15 \\ 1.13 \end{array} \right.$	$\left\{ \begin{array}{l} 3.29 \\ 3.30 \\ 3.25 \end{array} \right.$					
24.7 ... 74	30	$\left\{ \begin{array}{l} 93 \ 11 \\ 93 \ 1 \\ 93 \ 1 \end{array} \right.$	$\left\{ \begin{array}{l} 67 \ 30 \\ 68 \ 10 \\ 66 \ 55 \end{array} \right.$	$\left\{ \begin{array}{l} 1.45 \\ 1.41 \\ 1.47 \end{array} \right.$	$\left\{ \begin{array}{l} 3.26 \\ 3.27 \\ 3.23 \end{array} \right.$	1.44	3.25	65.0	4.68	-8.49
35.2 ... 77	0	$\left\{ \begin{array}{l} 82 \ 35 \\ 85 \ 23 \\ 82 \ 18 \end{array} \right.$	$\left\{ \begin{array}{l} 64 \ 11 \\ 65 \ 48 \\ 64 \ 42 \end{array} \right.$	$\left\{ \begin{array}{l} 1.70 \\ 1.66 \\ 1.67 \end{array} \right.$	$\left\{ \begin{array}{l} 3.26 \\ 3.46 \\ 3.26 \end{array} \right.$					
45.1 ... 76	30	$\left\{ \begin{array}{l} 88 \ 35 \\ 88 \ 55 \\ 87 \ 18 \end{array} \right.$	$\left\{ \begin{array}{l} 60 \ 7 \\ 60 \ 29 \\ 61 \ 9 \end{array} \right.$	$\left\{ \begin{array}{l} 2.04 \\ 2.02 \\ 1.94 \end{array} \right.$	$\left\{ \begin{array}{l} 3.33 \\ 3.36 \\ 3.30 \end{array} \right.$					
53.2 ... 76	0	$\left\{ \begin{array}{l} 90 \ 57 \\ 90 \ 33 \\ 90 \ 29 \end{array} \right.$	$\left\{ \begin{array}{l} 59 \ 15 \\ 59 \ 53 \\ 59 \ 54 \end{array} \right.$	$\left\{ \begin{array}{l} 2.08 \\ 2.03 \\ 2.03 \end{array} \right.$	$\left\{ \begin{array}{l} 3.29 \\ 3.29 \\ 3.29 \end{array} \right.$	2.05	3.29	59.3	6.75	6.62
64.9 ... 76	0	$\left\{ \begin{array}{l} 89 \ 37 \\ 89 \ 18 \\ 93 \ 4 \end{array} \right.$	$\left\{ \begin{array}{l} 59 \ 7 \\ 59 \ 27 \\ 58 \ 47 \end{array} \right.$	$\left\{ \begin{array}{l} 2.05 \\ 2.02 \\ 2.17 \end{array} \right.$	$\left\{ \begin{array}{l} 3.22 \\ 3.21 \\ 3.38 \end{array} \right.$					
76.0 ... 75	0	$\left\{ \begin{array}{l} 93 \ 39 \\ 96 \ 34 \\ 96 \ 15 \end{array} \right.$	$\left\{ \begin{array}{l} 61 \ 35 \\ 61 \ 6 \\ 61 \ 11 \end{array} \right.$	$\left\{ \begin{array}{l} 1.88 \\ 2.00 \\ 1.98 \end{array} \right.$	$\left\{ \begin{array}{l} 3.25 \\ 3.38 \\ 3.37 \end{array} \right.$					
85.5 ... 75	0	$\left\{ \begin{array}{l} 95 \ 22 \\ 95 \ 26 \\ 95 \ 16 \end{array} \right.$	$\left\{ \begin{array}{l} 61 \ 58 \\ 61 \ 56 \\ 62 \ 10 \end{array} \right.$	$\left\{ \begin{array}{l} 1.90 \\ 1.91 \\ 1.89 \end{array} \right.$	$\left\{ \begin{array}{l} 3.35 \\ 3.35 \\ 3.35 \end{array} \right.$	1.90	3.35	61.3	6.37	7.61
91.1 ... 75	0	$\left\{ \begin{array}{l} 95 \ 30 \\ 97 \ 16 \\ 97 \ 5 \end{array} \right.$	$\left\{ \begin{array}{l} 64 \ 21 \\ 63 \ 35 \\ 63 \ 41 \end{array} \right.$	$\left\{ \begin{array}{l} 1.76 \\ 1.86 \\ 1.85 \end{array} \right.$	$\left\{ \begin{array}{l} 3.43 \\ 3.51 \\ 3.50 \end{array} \right.$					
100	$\left\{ \begin{array}{l} 70 \ 0 \\ 75 \ 0 \\ 75 \ 0 \end{array} \right.$	$\left\{ \begin{array}{l} 115 \ 24 \\ 96 \ 47 \\ 96 \ 5 \end{array} \right.$	$\left\{ \begin{array}{l} 67 \ 43 \\ 66 \ 0 \\ 65 \ 2 \end{array} \right.$	$\left\{ \begin{array}{l} 1.67 \\ 1.69 \\ 1.73 \end{array} \right.$	$\left\{ \begin{array}{l} 3.48 \\ 3.56 \\ 3.49 \end{array} \right.$					

TABLE III.

Optical Constants of Copper-Nickel alloys. $\lambda=5461 \text{ \AA.}$

Atomic percent. nickel.	ϕ .	Δ .	2ψ .	n .	K.	Means. $\overbrace{n. \quad K.}$		R percent.	nK .	n^2-K .
	$^{\circ}$	$^{\circ}$	$^{\circ}$							
0 ... 70	0	$\left\{ \begin{array}{l} 86 \ 22 \\ 91 \ 1 \\ 90 \ 20 \end{array} \right.$	$\left\{ \begin{array}{l} 72 \ 57 \\ 73 \ 1 \\ 72 \ 2 \end{array} \right.$	$\left\{ \begin{array}{l} 0.773 \\ 0.819 \\ 0.858 \end{array} \right.$	$\left\{ \begin{array}{l} 2.15 \\ 2.35 \\ 2.31 \end{array} \right.$	$\left. \begin{array}{l} 0.817 \\ 2.27 \end{array} \right\}$		61.3	1.86	-4.49
8.8 ... 70	0	$\left\{ \begin{array}{l} 94 \ 37 \\ 98 \ 5 \\ 96 \ 44 \end{array} \right.$	$\left\{ \begin{array}{l} 71 \ 18 \\ 72 \ 43 \\ 72 \ 16 \end{array} \right.$	$\left\{ \begin{array}{l} 0.950 \\ 0.934 \\ 0.935 \end{array} \right.$	$\left\{ \begin{array}{l} 2.49 \\ 2.67 \\ 2.60 \end{array} \right.$	$\left. \begin{array}{l} 0.940 \\ 2.59 \end{array} \right\}$		64.1	2.43	-5.82
18.4 ... 72	30	$\left\{ \begin{array}{l} 96 \ 39 \\ 96 \ 6 \\ 95 \ 23 \end{array} \right.$	$\left\{ \begin{array}{l} 70 \ 48 \\ 70 \ 42 \\ 70 \ 27 \end{array} \right.$	$\left\{ \begin{array}{l} 1.14 \\ 1.16 \\ 1.16 \end{array} \right.$	$\left\{ \begin{array}{l} 3.06 \\ 3.02 \\ 2.98 \end{array} \right.$	$\left. \begin{array}{l} 1.15 \\ 3.02 \end{array} \right\}$		66.5	3.47	-7.80
24.7 ... 74	0	$\left\{ \begin{array}{l} 91 \ 25 \\ 90 \ 52 \\ 91 \ 17 \end{array} \right.$	$\left\{ \begin{array}{l} 66 \ 46 \\ 67 \ 51 \\ 67 \ 15 \end{array} \right.$	$\left\{ \begin{array}{l} 1.41 \\ 1.34 \\ 1.38 \end{array} \right.$	$\left\{ \begin{array}{l} 3.03 \\ 3.02 \\ 3.03 \end{array} \right.$	$\left. \begin{array}{l} 1.38 \\ 3.03 \end{array} \right\}$		62.8	4.18	-7.28
35.2 ... 76	0	$\left\{ \begin{array}{l} 83 \ 53 \\ 86 \ 42 \\ 83 \ 42 \end{array} \right.$	$\left\{ \begin{array}{l} 64 \ 32 \\ 66 \ 6 \\ 65 \ 10 \end{array} \right.$	$\left\{ \begin{array}{l} 1.59 \\ 1.55 \\ 1.55 \end{array} \right.$	$\left\{ \begin{array}{l} 3.07 \\ 3.26 \\ 3.07 \end{array} \right.$	$\left. \begin{array}{l} 1.56 \\ 3.13 \end{array} \right\}$		61.8	4.88	-7.36
45.1 ... 76	0	$\left\{ \begin{array}{l} 88 \ 41 \\ 89 \ 4 \\ 86 \ 42 \end{array} \right.$	$\left\{ \begin{array}{l} 60 \ 57 \\ 61 \ 29 \\ 62 \ 6 \end{array} \right.$	$\left\{ \begin{array}{l} 1.91 \\ 1.89 \\ 1.79 \end{array} \right.$	$\left\{ \begin{array}{l} 3.23 \\ 3.26 \\ 3.16 \end{array} \right.$	$\left. \begin{array}{l} 1.86 \\ 3.22 \end{array} \right\}$		59.9	5.99	-6.91
53.2 ... 76	0	$\left\{ \begin{array}{l} 88 \ 41 \\ 88 \ 4 \\ 88 \ 21 \end{array} \right.$	$\left\{ \begin{array}{l} 60 \ 6 \\ 60 \ 48 \\ 61 \ 15 \end{array} \right.$	$\left\{ \begin{array}{l} 1.96 \\ 1.91 \\ 1.89 \end{array} \right.$	$\left\{ \begin{array}{l} 3.20 \\ 3.19 \\ 3.22 \end{array} \right.$	$\left. \begin{array}{l} 1.92 \\ 3.20 \end{array} \right\}$		59.1	6.14	-6.55
64.9 ... 75	0	$\left\{ \begin{array}{l} 92 \ 22 \\ 92 \ 54 \\ 95 \ 14 \end{array} \right.$	$\left\{ \begin{array}{l} 59 \ 24 \\ 59 \ 26 \\ 58 \ 53 \end{array} \right.$	$\left\{ \begin{array}{l} 1.97 \\ 1.98 \\ 2.08 \end{array} \right.$	$\left\{ \begin{array}{l} 3.11 \\ 3.14 \\ 3.23 \end{array} \right.$	$\left. \begin{array}{l} 2.01 \\ 3.16 \end{array} \right\}$		57.9	6.35	-5.95
76.0 ... 74	0	$\left\{ \begin{array}{l} 95 \ 50 \\ 99 \ 53 \\ 99 \ 0 \end{array} \right.$	$\left\{ \begin{array}{l} 61 \ 43 \\ 61 \ 1 \\ 61 \ 7 \end{array} \right.$	$\left\{ \begin{array}{l} 1.81 \\ 1.97 \\ 1.93 \end{array} \right.$	$\left\{ \begin{array}{l} 3.11 \\ 3.30 \\ 3.26 \end{array} \right.$	$\left. \begin{array}{l} 1.90 \\ 3.22 \end{array} \right\}$		59.5	6.12	-6.76
85.5 ... 74	0	$\left\{ \begin{array}{l} 97 \ 16 \\ 98 \ 9 \\ 97 \ 57 \end{array} \right.$	$\left\{ \begin{array}{l} 62 \ 4 \\ 61 \ 47 \\ 62 \ 2 \end{array} \right.$	$\left\{ \begin{array}{l} 1.83 \\ 1.87 \\ 1.85 \end{array} \right.$	$\left\{ \begin{array}{l} 3.20 \\ 3.23 \\ 3.24 \end{array} \right.$	$\left. \begin{array}{l} 1.85 \\ 3.22 \end{array} \right\}$		60.0	5.96	-6.95
91.8 ... 74	0	$\left\{ \begin{array}{l} 97 \ 20 \\ 98 \ 22 \\ 98 \ 19 \end{array} \right.$	$\left\{ \begin{array}{l} 64 \ 29 \\ 64 \ 2 \\ 63 \ 36 \end{array} \right.$	$\left\{ \begin{array}{l} 1.69 \\ 1.74 \\ 1.77 \end{array} \right.$	$\left\{ \begin{array}{l} 3.28 \\ 3.32 \\ 3.30 \end{array} \right.$	$\left. \begin{array}{l} 1.73 \\ 3.30 \end{array} \right\}$		62.3	5.71	-7.90
100	$\left\{ \begin{array}{l} 70 \ 0 \\ 74 \ 0 \\ 74 \ 0 \end{array} \right.$	$\left\{ \begin{array}{l} 114 \ 6 \\ 98 \ 47 \\ 98 \ 52 \end{array} \right.$	$\left\{ \begin{array}{l} 67 \ 9 \\ 65 \ 42 \\ 65 \ 26 \end{array} \right.$	$\left\{ \begin{array}{l} 1.66 \\ 1.66 \\ 1.67 \end{array} \right.$	$\left\{ \begin{array}{l} 3.38 \\ 3.40 \\ 3.40 \end{array} \right.$	$\left. \begin{array}{l} 1.66 \\ 3.39 \end{array} \right\}$		64.2	5.63	-8.73

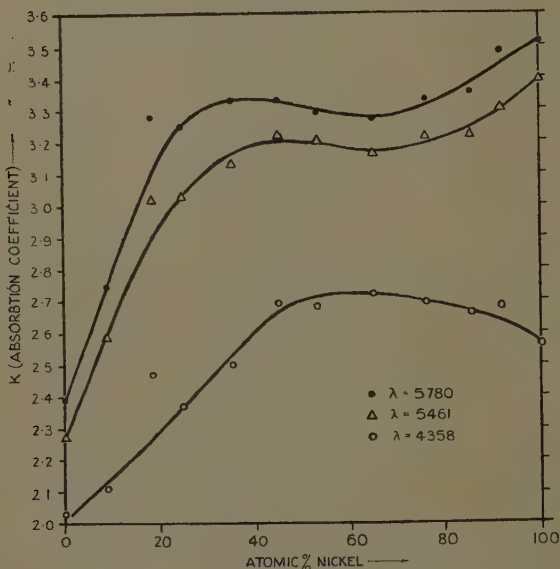
TABLE IV.

Optical Constants of Copper-Nickel Alloys. $\lambda=4358 \text{ \AA}$.

Atomic percent. nickel.	ϕ .	Δ .	2ϕ .	n .	K .	Means. $\left. \begin{array}{c} n. \\ K. \end{array} \right\}$		R. percent.	nK .	$n^2 - K^2$.
0 ... 67 0	0	$\begin{Bmatrix} 92 & 28 \\ 96 & 56 \\ 96 & 51 \end{Bmatrix}$	$\begin{Bmatrix} 67 & 22 \\ 68 & 22 \\ 68 & 12 \end{Bmatrix}$	$\begin{Bmatrix} 0.949 \\ 0.971 \\ 0.971 \end{Bmatrix}$	$\begin{Bmatrix} 1.91 \\ 2.09 \\ 2.08 \end{Bmatrix}$	0.964	2.03	51.6	1.96	-3.19
8.8 ... 67 0	0	$\begin{Bmatrix} 96 & 27 \\ 99 & 14 \\ 98 & 9 \end{Bmatrix}$	$\begin{Bmatrix} 65 & 42 \\ 68 & 42 \\ 67 & 19 \end{Bmatrix}$	$\begin{Bmatrix} 1.07 \\ 1.00 \\ 1.04 \end{Bmatrix}$	$\begin{Bmatrix} 2.03 \\ 2.17 \\ 2.12 \end{Bmatrix}$	1.04	2.11	51.7	2.20	-3.37
18.4 ... 70 0	0	$\begin{Bmatrix} 95 & 59 \\ 96 & 42 \\ 93 & 48 \end{Bmatrix}$	$\begin{Bmatrix} 68 & 27 \\ 68 & 14 \\ 67 & 30 \end{Bmatrix}$	$\begin{Bmatrix} 1.11 \\ 1.14 \\ 1.12 \end{Bmatrix}$	$\begin{Bmatrix} 2.50 \\ 2.53 \\ 2.38 \end{Bmatrix}$	1.12	2.47	57.7	2.77	-4.85
24.7 ... 70 0	0	$\begin{Bmatrix} 94 & 26 \\ 94 & 14 \\ 94 & 30 \end{Bmatrix}$	$\begin{Bmatrix} 65 & 2 \\ 65 & 47 \\ 65 & 28 \end{Bmatrix}$	$\begin{Bmatrix} 1.24 \\ 1.21 \\ 1.23 \end{Bmatrix}$	$\begin{Bmatrix} 2.36 \\ 2.37 \\ 2.38 \end{Bmatrix}$	1.23	2.37	53.6	2.92	-4.10
35.2 ... 73 0	0	$\begin{Bmatrix} 84 & 13 \\ 87 & 38 \\ 85 & 33 \end{Bmatrix}$	$\begin{Bmatrix} 62 & 22 \\ 65 & 56 \\ 65 & 32 \end{Bmatrix}$	$\begin{Bmatrix} 1.41 \\ 1.30 \\ 1.28 \end{Bmatrix}$	$\begin{Bmatrix} 2.39 \\ 2.61 \\ 2.51 \end{Bmatrix}$	1.33	2.50	54.4	3.33	-4.48
45.1 ... 73 0	0	$\begin{Bmatrix} 91 & 8 \\ 91 & 29 \\ 88 & 14 \end{Bmatrix}$	$\begin{Bmatrix} 63 & 6 \\ 63 & 47 \\ 64 & 16 \end{Bmatrix}$	$\begin{Bmatrix} 1.51 \\ 1.48 \\ 1.39 \end{Bmatrix}$	$\begin{Bmatrix} 2.71 \\ 2.74 \\ 2.61 \end{Bmatrix}$	1.46	2.69	56.1	3.93	-5.10
53.2 ... 73 0	0	$\begin{Bmatrix} 91 & 3 \\ 90 & 41 \\ 91 & 13 \end{Bmatrix}$	$\begin{Bmatrix} 62 & 31 \\ 62 & 34 \\ 61 & 47 \end{Bmatrix}$	$\begin{Bmatrix} 1.54 \\ 1.53 \\ 1.58 \end{Bmatrix}$	$\begin{Bmatrix} 2.69 \\ 2.68 \\ 2.68 \end{Bmatrix}$	1.55	2.68	54.7	4.15	-4.78
64.9 ... 73 0	0	$\begin{Bmatrix} 92 & 6 \\ 91 & 56 \\ 94 & 8 \end{Bmatrix}$	$\begin{Bmatrix} 60 & 8 \\ 60 & 52 \\ 61 & 4 \end{Bmatrix}$	$\begin{Bmatrix} 1.68 \\ 1.64 \\ 1.68 \end{Bmatrix}$	$\begin{Bmatrix} 2.68 \\ 2.69 \\ 2.79 \end{Bmatrix}$	1.67	2.72	54.0	4.54	-4.61
76.0 ... 71 0	0	$\begin{Bmatrix} 97 & 54 \\ 102 & 0 \\ 100 & 54 \end{Bmatrix}$	$\begin{Bmatrix} 61 & 20 \\ 61 & 13 \\ 60 & 59 \end{Bmatrix}$	$\begin{Bmatrix} 1.57 \\ 1.69 \\ 1.67 \end{Bmatrix}$	$\begin{Bmatrix} 2.59 \\ 2.76 \\ 2.71 \end{Bmatrix}$	1.64	2.69	53.8	4.41	-4.55
85.5 ... 71 0	0	$\begin{Bmatrix} 99 & 35 \\ 100 & 18 \end{Bmatrix}$	$\begin{Bmatrix} 61 & 6 \\ 60 & 31 \end{Bmatrix}$	$\begin{Bmatrix} 1.63 \\ 1.67 \end{Bmatrix}$	$\begin{Bmatrix} 2.65 \\ 2.67 \end{Bmatrix}$	1.65	2.66	53.2	4.39	-4.35
91.8 ... 71 0	0	$\begin{Bmatrix} 98 & 32 \\ 99 & 0 \\ 100 & 18 \end{Bmatrix}$	$\begin{Bmatrix} 63 & 0 \\ 62 & 9 \\ 62 & 7 \end{Bmatrix}$	$\begin{Bmatrix} 1.50 \\ 1.56 \\ 1.59 \end{Bmatrix}$	$\begin{Bmatrix} 2.66 \\ 2.66 \\ 2.72 \end{Bmatrix}$	1.55	2.68	54.7	4.15	-4.78
100	$\begin{Bmatrix} 70 & 0 \\ 71 & 0 \\ 71 & 0 \end{Bmatrix}$	$\begin{Bmatrix} 96 & 52 \\ 97 & 28 \\ 97 & 21 \end{Bmatrix}$	$\begin{Bmatrix} 63 & 47 \\ 63 & 50 \\ 63 & 36 \end{Bmatrix}$	$\begin{Bmatrix} 1.35 \\ 1.44 \\ 1.44 \end{Bmatrix}$	$\begin{Bmatrix} 2.44 \\ 2.64 \\ 2.61 \end{Bmatrix}$	1.41	2.56	54.4	3.61	-4.57

The non-linearity of these curves and the pronounced maxima and minima which occur must be intimately associated with the dispersion curve of copper, which has a sharp minimum in the visible region of the spectrum near the yellow. It is for this reason that the greatest variations of optical constants are shown for yellow light. This is well illustrated by the reflecting power curve, which for the yellow has an exceedingly high value for

Fig. 3.

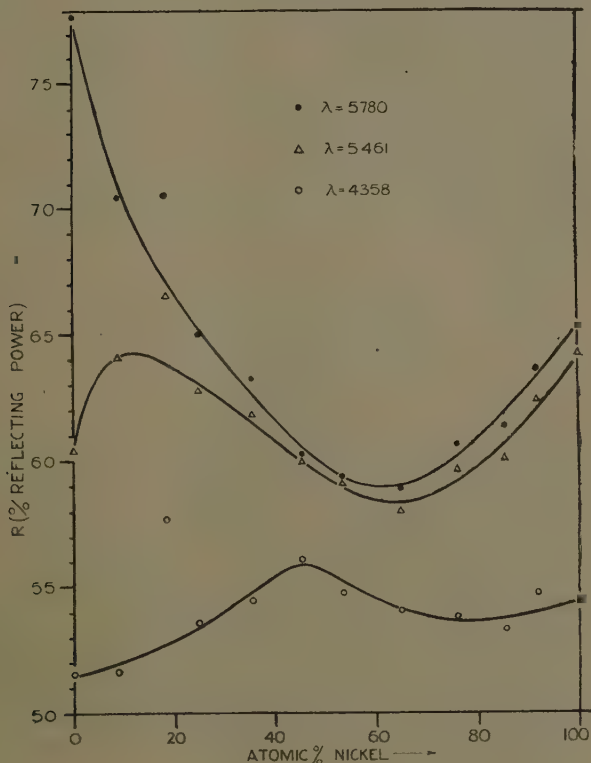


copper, decreasing sharply to a minimum at 60 per cent. and increasing again to nickel. The maxima for the other two wave-lengths occur at 10 and 45 per cent., and the minima at 65 and 85 per cent. It will be noticed that the minima for the reflecting power curves occur at exactly the same compositions as the maxima for the $n^2 - K^2$ curves.

All the curves are characterized by the shift of the maxima and minima towards the nickel end with

decreasing wave-length. This again must be a consequence of the dispersion of copper combined with the uniform dispersion of nickel, which shows a steady decrease in the values of the optical constants as the

Fig. 4.



wave-length decreases. We should expect that in regions far removed from "anomalous" dispersion, such as the ultra-violet, the constants should vary linearly with composition.

(Note that the maxima and minima for violet are very much flattened compared with the other wave-lengths.)

Fig. 5.

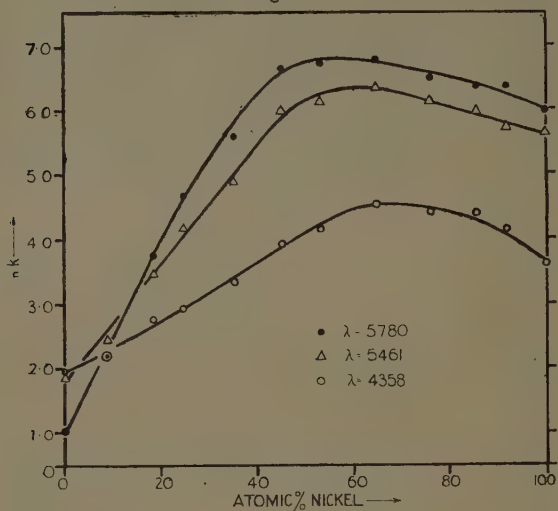
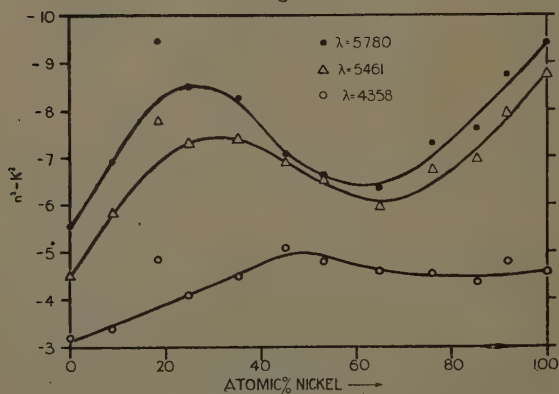


Fig. 6.



On the other hand, even greater variations should occur in the red and near infra-red in which region the minimum in the dispersion of copper occurs. It is clear

that measurements over a much wider wave-length range extending from the ultra-violet to the near infra-red are very desirable, and an attempt to do this is being made, using a photo-electric apparatus.

A glance at the absorption coefficient/composition curve will show that the 18.8 per cent. alloy has abnormally high values for all three wave-lengths. This particular specimen was imperfect and had a large number of pin-holes in the surface, but was included because it was the best specimen in this range. It lies well, however, on the refractive index curve. This is what might be expected, for owing to repeated reflexions in the tiny cavities and thus to multiple absorption, the value of K would be increased, but no such effect would occur with the refractive index. Similar abnormally high values are shown for the $n^2 - K^2$ and R curves, but not for the nK curve.

Since K is abnormally large for this specimen it follows that the value of R calculated from

$$R = \frac{n^2 + K^2 + 1 - 2n}{n^2 + K^2 + 1 + 2n},$$

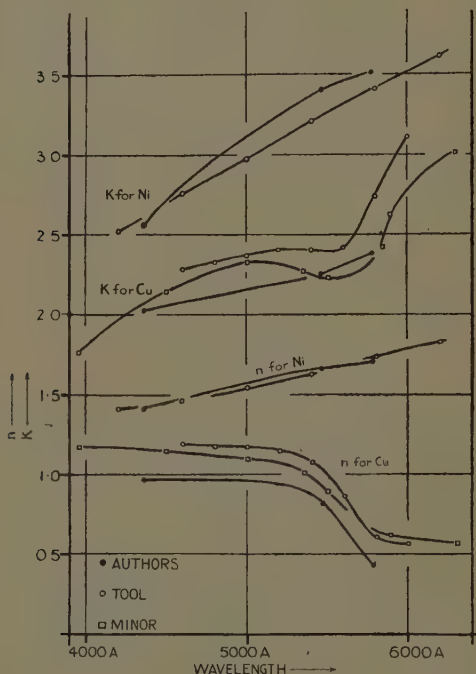
must also be abnormally large, as the curve indicates. It is, however, interesting to note that if the reflecting power of this same alloy had been measured by normally reflected light, the same cause, the pinholes, would have produced an abnormally low value for the reflecting power.

The dispersion curves for copper and nickel show a general parallelism with those of Tool ⁽²³⁾ and Minor ⁽²⁶⁾ (fig. 7). This, as Tool remarks, has been a common experience with sets of independent results, and is almost certainly due to differences in polishing. It has been observed that burnished and heavily flowed surfaces result in higher values of n . Tool and Minor burnished their surfaces. Presumably then the lower results of the authors may be taken as an indication of some success in avoiding this type of surface with copper and the softer alloys which flow readily. The dispersion curve for nickel differs only slightly from Tool's result. Large differences would not be expected in the case of harder metals which do not flow easily.

It is worth pointing out that while the electrical conductivity for these three frequencies ($nK\nu$) rises to a

maximum, the electrical conductivity for direct currents falls to a minimum. Further, the minimum value of the "optical" electrical resistance is about 250 microhms/c.c., whilst the maximum value of the "direct" specific resistance is about 50 microhms/c.c.

Fig. 7.



IV. Previous Work.

The only previous investigation on the optical constants of these alloys is that of Littleton⁽²⁷⁾ who, in 1911, studied the optical constants of alloys as a function of composition, dealing particularly with the various series iron-nickel, nickel-silicon, iron-manganese, aluminium-copper, and copper-nickel. He was well acquainted with the difficulties of the work, especially with regard to

obtaining suitable polished surfaces and the preparation of homogeneous alloys. His experimental method was that of Drude using the Soleil modification of the Babinet compensator.

A strict comparison between his work for the copper-nickel series and the present is not possible for the following reasons:—In Littleton's work, (1) light of one wave-length only was used, viz., sodium light; (2) only five specimens over the whole range were measured; (3) only one determination of the optical constants was made for each alloy; (4) the method of polishing adopted is now known to be inefficient in producing uncontaminated surfaces of constant optical quality (mainly on account of the use of rouge); (5) the mode of preparation of the specimens was inadequate. On the last point it may be remarked that, in order to obtain homogeneous alloys, he maintained his specimens in the molten state for four hours and allowed them to cool over night. This procedure does not prevent cored structure with the copper-nickel alloys, as the coring occurs during solidification. The only effective method of producing homogeneity is by prolonged annealing at as high a temperature as possible.

V. *Summary.*

The optical constants of the copper-nickel alloys have been measured by a polarimetric method for twelve specimens for the wave-lengths 5780 Å., 5461 Å., and 4358 Å. Measurements for each specimen have been repeated three times, and consistent results obtained. Stress is laid on the method of polishing adopted which aims at the production of a very thin flowed layer. Curves of the constants n , K , R , nK , and $n^2 - K^2$ against atomic percentage composition for the three wave-lengths are shown and discussed, and certain of their features pointed out.

VI. *Bibliography.*

- (1) Guertler and Tamman, *Zeits. Anorg. Chem.* lii. p. 25 (1907).
- (2) Feussner, *Abh. Phys. Reichsanstalt*, ii. p. 503 (1895); Krupowski, *R. v. Met.* xxvi. p. 142 (1929).
- (3) Smith, *Ohio Univ. Bull.* ii. no. 7 (1925).
- (4) Feussner, *Abh. Phys. Reichsanstalt*, ii. p. 501 (1895).
- (5) Sacklowski, *Ann. Phys.* lxxvii. p. 241 (1925).
- (6) Graber, *Phys. Rev.* xxvi. p. 380 (1925).

- (7) C. V. Kent, *Phys. Rev.* xiv. p. 459 (1919).
- (8) Drude, *Ann. d. Phys.* xxxix. p. 481 (1890).
- (9) Jay, *Journ. Iron & Steel Inst.* i. p. 427 (1932).
- (10) Adcock, *Trans. Farad. Soc.* xxvi. p. 544 (1930).
- (11) Archbutt, *Journ. Inst. Metals*, xxxiii. p. 227 (1930); Allen, *ibid.* xliii. p. 81 (1930).
- (12) Belaiew, 'Crystallisation of Metals,' p. 46 (1922).
- (13) Weiss and Henry, *Comptes Rendus*, clxxi. p. 108 (1920), clxxiv. p. 1421 (1922), and clxxv. p. 1402 (1922); Carpenter and Smith, *Journ. Inst. Metals*, xxix. p. 29 (1923).
- (14) Bruni and Meneghini, *Inst. Zeit. Metallographie*, clxxi. p. 108 (1920).
- (15) Beilby, 'Aggregation and Flow of Solids,' p. 85 (1921).
- (16) Macaulay, *Journ. Royal Technical Coll., Glasgow*, ii. (1931).
- (17) G. P. Thomson, *Proc. Roy. Soc. A*, cxxviii. p. 750 (1930).
- (18) Finch, Quarrel, and Roebuck, *Proc. Roy. Soc. A*, xlv. p. 676 (1934).
- (19) Blackman, *Phil. Mag.* xviii. p. 262 (1934).
- (20) Margenau, *Phys. Rev.* xxxiii. p. 639 (1929).
- (21) Lowery and Moore, *Phil. Mag.* xiii. p. 938 (1932); Drude, *Ann. Phys.* xxxvi. p. 532 (1889).
- (22) Mott and Zener, *Proc. Camb. Phil. Soc.* xxx. p. 249 (1934).
- (23) Tool, *Phys. Rev.* xxxi. p. 1 (1910).
- (24) French, *Proc. Roy. Soc. A*, cxl. p. 637 (1933).
- (25) Wheeler, *Amer. Journ. Sci.* xxxv. p. 491 (1913).
- (26) Minor, *Ann. Phys.* x. p. 581 (1903).
- (27) Littleton, *Phys. Rev.* xxxiii. p. 453 (1911).
- (28) Kirk Rose, *Journ. Inst. Metals*, xviii. p. 86 (1912).

XXIX. Notices respecting New Books.

The Calculation of Variations in the Large. By MARSTON MORSE. [368 pages.] (American Mathematical Society. Colloquium Publications.—Vol. XVIII. New York, 1934. Price \$4.50.)

THIS book is exceptional in that it is the product of its author's own research and yet is broad in its outlook. Professor Morse has worked for the last ten years on functional analysis in the large, or, as he aptly terms it, macro-analysis. He first was concerned with the theory of the critical points of a function of position on a Riemannian Manifold (a critical point is a point at which the gradient of the function vanishes); this work is given in Chapter VI. of the present volume, and it may be mentioned that a part of this is work to be studied by all algebraic geometers. From the macro-analysis of functions Professor Morse turned to the macro-analysis of the functionals of the Calculus of Variations, and the volume in hand is an exposition of this later work.

The author devotes his first four chapters to the classical results of the Calculus of Variations, where the word classical may be taken to mean independent of combinatory topology; his account is well arranged, and he covers a great deal of ground

in a hundred pages. His fifth chapter he uses as an intermediary chapter: it presents the results and ideas of the previous chapters in the tensor form for applications to the Riemannian Manifold. Chapter VI., as we have already said, is devoted to the macro-analysis of functions, and the next two chapters develop the corresponding results for functionals. The concluding chapter contains the application of Professor Morse's ideas to the Continuation Problem of Poincaré, and the solution bears witness to the power of the author's methods.

The book has been well printed by the Waverley Press of Baltimore, Md.

Fourier Transforms in the Complex Domain. By the late R. E. A. C. PALEY and NORBERT WIENER. (American Mathematical Society. Colloquium Publications.—Vol. XIX. New York, 1934. Price \$3.)

THIS volume contains the results of a year's collaboration cut tragically short by the death of the first-named author. Their subject is a development of the Fourier Transform theory, which owes so much in its recent advances to Wiener. Expectations from such far-reaching minds as those of these authors are not disappointed in this volume, and it is not without human and mathematical interest that one reads in Wiener's introduction, "We had worked together with a blackboard before us and, when we had covered it with our joint comments, one or other of us would copy down what was relevant and reduce it to preliminary written form." Such is the origin of this book: the final editing has been done by Wiener.

Just as Wiener's book on the Fourier Integral attracts by his coordination of Taberian Theorems which were previously disconnected save in type of result, each possessing its own *ad hoc* proof, so does this work set forth a multitude of subjects handled by the Fourier Transform. It is impossible here to do more than give a list of subjects treated, and an incomplete list at that: Quasi-analytic Functions, Integral Equations, Integral Functions of exponential type, Lacunary Series, Harmonic Analysis in the complex plane, Random Functions.

Much that is given in the book is not new as regards results, but it is all new as regards correlated presentation and proof; and in modern analysis mathematicians have cause enough to feel that coordination of previously disconnected matter is an advance of importance.

The work has been carefully done, is well arranged, and attractively presented. Its technical production is of the standard of its mathematical interest.

Bulletin of the National Research Council, No. 90. *Physics of the Earth*.—VI. *Seismology*. (Published by the National Research Council of The National Academy of Sciences, Washington, D.C. Paper \$2.00. Cloth \$2.50.)

A SUBJECT with ill-defined boundaries and closely linked with certain well-developed sciences is apt to be at a disadvantage until its status is established and its domain well marked out; it suffers by being everybody's business or, perhaps, nobody's business. Geophysics in general, and seismology in particular, are instances. It was the recognition that the No Man's Land between the more popularly recognized aspects of science (which still suffers from its traditional division into "subjects" or "branches") needed exploring in greater detail that led to the organizing by the National Research Council of the National Academy of Sciences, Washington, of a strong committee charged with preparing a series of monographs or bulletins on the Physics of the Earth, each the special work of a special subcommittee.

The work under notice is the bulletin dealing with Seismology. Unquestionably the subcommittee, under the chairmanship of Fr. J. B. Macelwane, S.J., have done their work well, and subject-matter of the chapters, each written by a specialist of world-wide repute, leaves little to criticize from the seismological standpoint. The typography is good, and the references, which form a short bibliography at the end of each chapter, are well-discriminated—a great achievement—for in seismology particularly it would be a blemish if too few or too many references were given.

The subdivision into chapters has been well carried out, an indication of good staff-work and editorial management. It is a matter for regret that the chairman seems to have generously exercised a self-denying ordinance, and, by curtailing his own contributions, he has rather thrown the book out of balance in places. For instance, there is a valuable critical chapter by H. O. Wood on Volcanic Earthquakes that occupies twenty-two pages: the author has gone a long way towards clearing many of the controversial questions of volcanic earthquakes, particularly in distinguishing carefully between volcanic earthquakes and tectonic earthquakes that occur in a volcanic region such as Hawaii; yet on the subject of the Reflection and Refraction of Earthquake Waves Fr. Macelwane limits himself to four pages and gives only a theoretical outline of the method without even summarizing the interesting and unexpected relations between the amplitudes of the reflected and refracted waves. Two pages less would scarcely have impaired the former article on volcanic earthquakes; two extra pages, showing graphically

how much energy is reflected or transformed at different angles of incidence would have made the latter chapter of considerably greater value for seismologists.

It is invidious to single out particular sections for praise, so well have the respective authors carried out their task; it would merely indicate the predominant interest of the reviewer. The instrumental seismologist will naturally appreciate J. A. Anderson's exposition of the principle of the seismograph and Prof. Byerly's chapters on the reading and analysis of seismograms and on time-distance curves, whereas the geophysicist (using the word in a rather narrow sense) will tend to concentrate on "The Mechanics of Earthquakes" (by H. Fielding Reid) and Macelwane's chapters on wave propagation. The geologist will presumably turn to the sections by Wood and Macelwane that could be classified roughly as "field methods." Any such clear-cut division, however, would be unfortunate, and the occasional overlapping of chapters (for which the editor apologizes in the preface) is a healthy sign that modern specialization has not obliterated the comprehensive view that seismology needs perhaps more than most subjects.

Fr. Macelwane has done a great service in giving an account in English of Karl Uller's theory of wave-propagation. Again, there is reason to regret his editorial self-denial, for there is no indication as to whether the different kinds of waves that the Uller theory requires can be propagated to great distances, whether they are diffracted along a discontinuity, or whether they are transient; nor are the different types compared and contrasted with the wave-types predicted by the customary theory of wave-velocity and group-velocity. Macelwane is needlessly pessimistic about the use of Love wave observations to determine the thickness of surface layers; the fact that Love waves can exist when the transition in properties in the crust is continuous does not invalidate the application of the method to problems in which there is ample evidence to show that the transition is very rapid, if not quite abrupt.

Finally, it ought to be mentioned that the freshness of treatment of the different topics, at the risk of omitting some items that a work of reference would often contain, makes this bulletin, in common with the other bulletins that have appeared, a welcome contrast to the uncritical (and hence uninspiring) encyclopædic compilations that are of questionable value to the expert, possibly misleading to the worker in another subject, and unilluminating to the general reader. The editor and his collaborators deserve the congratulations and thanks of all seismologists.

Introduction to Atomic Spectra. By H. E. WHITE. [Pp. xii + 457.] (London: McGraw-Hill, 1934. Price 30s.)

THIS book inevitably goes over much of the ground which has been well surveyed in its predecessors, of which there are two, with not very dissimilar aims, in this same International Series of Physics. It cannot be said, therefore, to fill a glaring gap in the literature of atomic physics; but in a subject which has developed so rapidly—and which is still developing, though at a less hectic speed—there is room for a book in which accounts of the most recent work are incorporated, and in which a wider range of observational material can be drawn upon in the selection of appropriate illustrative data. Moreover, a stage has now been reached at which an account can be given of the interpretation of line spectra which is unlikely to call for revision in a few months time.

The aim of the author has been to begin at the beginning of each topic, so that the student will have no undue difficulty in following the treatment as it is developed in connexion with the more intricate questions. This modestly named 'Introduction' is so complete within its self-imposed limits that it is simpler to state what is not dealt with rather than what is. Detailed derivations of the more elaborate theoretical formulæ are not given, though the methods are indicated; there are no systematic lists of wave-lengths or of term values, though there is much illustrative data; and the experimental technique of spectroscopy is not considered.

It is pleasant to find, in the first chapter, due recognition paid to the fact that quite a considerable amount of work was done on spectroscopy before 1913! The essentials of the orbital and quantum mechanical treatments of atomic structure are well described, the relations between them being brought out very clearly with the aid of eigenfunction and charge distribution diagrams. The simpler questions are then dealt with, including the series relations, fine structure, and Zeeman effect in spectra of one electron systems. The treatment is developed in stages, next for two electron systems, and finally, generally, for more complex systems. X-rays, iso-electronic sequences, hyperfine structure, and the Stark effect are all discussed in detail, and there are excellent chapters on series perturbations and the breadth of spectral lines—subjects which are often avoided! The presentation throughout is extremely clear, and, in spite of the completeness with which the subject is treated, the essential matters are not obscured by a mass of detail.

The author has spared no pains in preparing numerous useful diagrams of energy level systems, multiplet and hyper-

fine structures, and, Zeeman patterns, as well as others which bring out vividly the results of theoretical calculations; and there is an abundance of reproductions of spectrograms, many of them original, which illustrate, often in a novel and striking manner, all the main topics which are considered.

The book is a valuable addition to the literature of atomic spectra which will be indispensable to those who wish to study the subject in any detail; for physicists with a general interest in the subject, and students who, perhaps, cannot devote as much time to a particular topic as this book as a whole would require, it may be strongly recommended, if only for the excellence of the diagrams and photographs.

Principles of Mathematical Physics. By W. V. HOUSTON.
[Pp. xi+265.] (London: McGraw-Hill, 1934. Price 21s.)

THIS book deals with a wide range of subjects in the field of classical mathematical physics in a form suitable for honours students. On a more purely mathematical side there are chapters on differential equations, the calculus of variations, and vector analysis. Under mechanics, Hamilton's principle and the general theory of vibrating systems are treated, as well as the more elementary topics. The basic principles of thermodynamics and statistical mechanics are presented, and the final chapters deal with electrostatics, electromagnetic theory, and special relativity.

The covering of so wide a range in a comparatively short space is made possible only by the special method adopted, which may be fairly indicated by the following extracts from the preface:—"In general, the idea has been to emphasize the derivation of results from explicitly stated postulates and to distinguish carefully between such derivation and physical intuition . . . The book has been written as a text, not as a treatise, and as much as possible has been left to the resourcefulness of the student. The physical theory is presented only in the barest outline. . . The details of the theory are left for the student to fill in by solving the problems." The general programme has been well carried out. In the statements of the postulates the essentials have been seized upon and presented briefly and clearly. The problems are well chosen and, if they were worked through, a fairly extensive survey would be gained of the ground usually covered in the books dealing with the various special subjects.

As the preface admits, however, "This form of presentation makes severe demands upon both the student and the instructor." The statement summarizes a criticism of the value of the book which can hardly be avoided. Practically

all of the material is contained in readily accessible standard books on the various special topics; the student must make use of these if he is to gain more than a superficial appreciation of most of the topics treated; and, in so far as he does use them, this book becomes less necessary. This, however, is an external criticism; judged from the point of view of the purpose professed by the author the book is admirable. It will undoubtedly be useful both to students and "instructors" as a guide for the planning of their work, and for purposes of revision. It would be more widely appreciated if the price were considerably less.

Lectures on Matrices. By J. H. M. WEDDERBURN. [Pp. vii+200.] (American Mathematical Society. Colloquium Publications.—Vol. XVII. New York, 1934. Price \$3.)

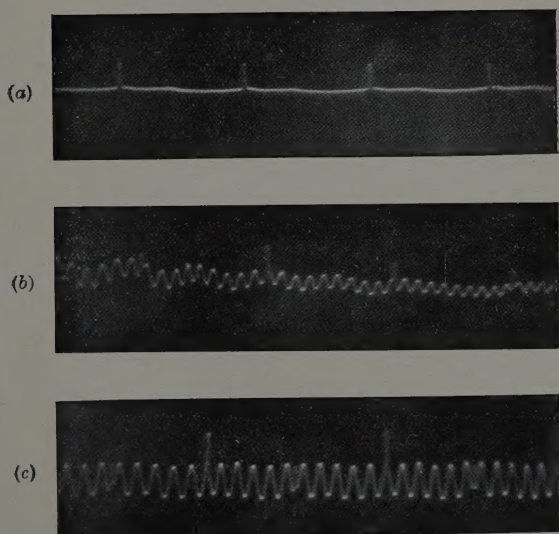
THE theory of matrices is one of the most vigorous branches of mathematics at the present time, and one can welcome unreservedly this volume by an author, who has himself so notably advanced the subject. It contains the substance of lectures given over a number of years, and has, therefore, been shaped by the test of actual teaching. It assumes no previous knowledge of matrix theory, and does not deal with applications to other subjects, but will place the reader in a position to follow with profit the most recent investigations in this branch of algebra.

The first three chapters survey the fundamental properties of matrices, leading up to their expression in normal form, and the determination of matrices with given elementary divisors. Chapters follow on singular matrix polynomials, compound matrices, and matrices of special types. A chapter on functions of matrices includes recent developments on the differentiation of functions of a variable matrix, work with important applications in quantum theory. The final chapter is in some ways the most interesting. Starting with a brief, but admirable, sketch of *algebras* in general, it discusses the representation of an associative algebra as a matrix algebra, the theory of sub-algebras, and the classification of algebras.

Mention must be made of the excellent bibliography. This, while not professing to be complete, appears to include in its five hundred and forty-nine items every paper of importance which has appeared up to the end of 1933. The printing and paper are first-rate, and only a few trivial errata have been observed.

[The Editors do not hold themselves responsible for the views expressed by their correspondents.]

FIG. 2.



Records of (a) Time-marker alone; (b) time-marker with vibration from asbestos cement sheet 7 in. long; (c) time-marker with vibration from steel bar 18 in. long.

